

**FIELD SAMPLING PLAN
FOR THE
DSC-GIBRALTAR SITE
GIBRALTAR, WAYNE COUNTY, MICHIGAN**

Prepared for

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Region V

Prepared by

WESTON SOLUTIONS, INC.
Region V Superfund Technical Assessment and Response Team

November 11, 2009

Approved by: _____ Date: _____
U.S. EPA Region V
On-Scene Coordinator

Project Dates of Sampling:	November 16, 17, 2009
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ACRONYM LIST

BOD	Biological Oxygen Demand
COC	Chain-of Custody
COD	Chemical Oxygen Demand
CWLF	County Wide Landfill
DCR	Detroit Cold Rolling
DSC	Detroit Steel Company
DSCG	Detroit Steel Company Gibraltar
ERB	Emergency Response Branch
ERRS	Emergency Rapid Response Services
EQM	Environmental Quality Management, Inc.
FSP	Field Sampling Plan
GPS	Global Positioning System
MS/MSD	Matrix Spike/Matrix Spike Duplicate
NPDES	National Pollution Discharge Elimination System
OSC	On-Scene Coordinator
PCB	Polychlorinated Biphenyl
PID	Photoionization Detector
PPE	Personal Protective Equipment
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
FSP	Field Sampling Plan
SOP	Standard Operating Procedure
SVOC	Semi-volatile Organic Compound
START	Superfund Technical Assessment and Response Team
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
U.S. EPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound
WESTON	Weston Solutions, Inc.

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1.0 Introduction

This Field Sampling Plan (FSP) identifies the data collection activities and associated quality assurance/quality control (QA/QC) measures specific to the Detroit Steel Company (DSC)-Gibraltar Facility Site (the Site) located in Gibraltar, Wayne County, Michigan. All data will be generated in accordance with the quality requirements described in the *START III Generic QAPP*, dated June 2006. The purpose of this FSP is to describe site-specific tasks that will be performed in support of the stated objectives. The FSP will reference the QAPP for generic tasks common to all data collection activities including routine procedures for sampling and analysis, sample documentation, equipment decontamination, sample handling, data management, assessment, and data review. Additional site-specific procedures and/or modifications to procedures described in the *START III Generic QAPP* are described in the following FSP elements.

This FSP is prepared, reviewed, and approved in accordance with the procedures detailed in the *START III Generic QAPP*. Any deviations or modifications to the approved FSP will be documented using **Table 1: FSP Revision Form**.

2.0 Project Management and FSP Distribution and Project Team Member List

Management of the Site will be as documented in the *START III Generic QAPP*. Refer to the *START III Generic QAPP* for an organizational chart, communication pathways, personnel responsibilities and qualifications, and special personnel training requirements.

The following personnel will be involved in planning and/or technical activities performed for this data collection activity. Each will receive a copy of the approved FSP. A copy of the FSP will also be retained in the site file.

Personnel	Title	Organization	Phone Number	Email
Brian Kelly	OSC	U.S. EPA	(734) 740-9019	Kelly.Brian@epamail.epa.gov
Alex Clark	Project Manager	START	(248) 200-9825	A.Clark@Westonsolutions.com
John Wentz	Project Engineer	EQM	(513) 673-4050	jwentz@eqm.com
Eric Bowman	Response Manager	EQM	(513) 265-8875	ebowman@eqm.com
Sam Bugg	Chemist	EQM	(513) 543-0578	sbugg@eqm.com
Angye Dragotta	Chemist	EQM	(513) 742-7256	adragotta@eqm.com
Tonya Balla	Health and Safety	START	(847) 918-4094	T.Balla@Westonsolutions.com
Lisa Graczyk	QA Reviewer	START	(312) 424-3339	L.Graczyk@Dynamac.com

NOTES:

OSC – On-Scene Coordinator
 QA – Quality Assurance

START – Superfund Technical Assessment and Response Team
 U.S. EPA – United States Environmental Protection Agency

3.0 Planning and Problem Definition

3.1 Problem Definition

The Site is the former Detroit Cold Rolling (DCR) and McLouth Steel facility located at 28000 W. Jefferson Avenue in Gibraltar, Wayne County, Michigan, (Figure 3-1) and was referred to the United States Environmental Protection Agency (U.S. EPA) Region V Emergency Response Branch (ERB) by the Michigan Department of Environmental Quality (MDEQ) for consideration in developing an on-site leachate treatment system at the Site to treat the combined leachate streams from four landfills to meet National Pollution Discharge Elimination System (NPDES) requirements associated with discharge to the Frank and Poet Drain.

The U.S. EPA On-Scene Coordinator (OSC) has tasked the Superfund Technical Assessment and Response Team (START) contractor Weston Solutions, Inc. (WESTON®) and the Emergency Rapid Response Services (ERRS) contractor Environmental Quality Management Inc. (EQM) with on-site data collection for design and construction of a leachate treatment system and sample collection of liquids from available access points in the existing leachate collection system associated with Landfills 1A and 1B at the Gibraltar Facility Site as well as for County Wide Landfill (CWLF). A site features map is provided (Figure 3-2).

3.2 Site History and Background

The waste buried in Landfills 1A and 1B is steel mill waste from historic operations of the former McLouth Steel at the site. A landfill was constructed at the CWLF to the west of the Site that also accepted steel mill waste; this landfill is designated the lower CWLF. After that landfill no longer accepted steel mill waste, another landfill was constructed on top of the lower CWLF, which is designated the upper CWLF. The upper CWLF is a construction and demolition (C&D) debris landfill. Both landfills have rudimentary leachate collection systems in place, but are in need of a more comprehensive/long-term leachate management/treatment system.

In December 2008, MDEQ requested assistance from U.S. EPA for development of a leachate collection and treatment system for Landfills 1A and 1B and CWLF

3.3 Contaminants of Concern/Target Analytes

The following is the list of target analytes and/or classes of compounds that will be analyzed for pre-design considerations:

1. Total Metals
2. Dissolved Metals
3. Full List Semivolatile Organic Compound (SVOC)
4. Full List Volatile Organic Compound (VOC)
5. Pesticides
6. Polychlorinated Biphenyl (PCB)

7. Ammonia as Nitrogen
8. Biological Oxygen Demand (BOD)
9. Chemical Oxygen Demand (COD)
10. Total Suspended Solids (TSS)
11. Total Solid (TS)
12. Total Dissolved Solids (TDS) (by calculation)
13. Oil and Grease (O & G)
14. Cyanide
15. Bicarbonate
16. Carbonate
17. Phosphorus
18. Total Organic Carbon (TOC)
19. Sulfates
20. Chloride
21. Hardness
22. Fluoride
23. Nitrate/Nitrite
24. Acute Toxicity (48 hrs screen both species)
25. Low Level Mercury

4.0 Project Description and Schedule

The following tasks were requested by the OSC and are anticipated to be completed during two days of field activities the week of November 16, 2009:

- **Task 1 – Sample collection DSC 1A & 1B**
 - Allow wastewater treatment operator to pump down each sump. Pump volumes may be limited by the volume the receiving pond is able to accept. “Purging” will be considered complete when the operator has removed as much water as possible or 3 times the calculated volume, whichever occurs first.
 - Collect air monitoring readings, as necessary.
 - Collect liquid sample of representative leachate from both fill areas as a direct sample from a pressurized line either at a sample tap or at the pipe discharge or alternatively at a well with a submersible centrifugal, variable speed pump or bailers after purging activities.
- **Task 2 – Sample collection County Wide Landfill (CWLF) Upper**
 - Confirm stand pipes have been purged within last 24 hours. Purging will consist of the landfill personnel performing the routine vacuum collection of the liquid from each standpipe. Vacuum purging is to be performed within 24-hours prior to the sample collection.
 - Collect air monitoring readings of the headspace at the top standpipes to be sampled.
 - Collect liquid level measurement at each standpipe to be sampled.
 - Collect liquid leachate samples with submersible centrifugal, variable speed pump or bailers.

- **Task 3 – Sample collection CWLF Lower**
 - Collect air monitoring readings of the headspace at the top of the wells to be sampled.
 - Collect liquid level measurement at each well to be sampled.
 - Attempt to purge 3 well volumes from each well to be sampled.
 - Collect liquid leachate samples with submersible centrifugal, variable speed pump or bailers.

START and ERRS will have 3-4 persons (total) on-site to perform the sampling and sample management. The sample management will consist of labeling and documenting the samples for shipment to the laboratory. Sample collection will need to be completed by 1500 hours on each day as lab courier pickup is scheduled for 1530 hours.

Sample labels and chain-of-custody (COC) paperwork will be generated by WESTON START and/or ERRS personnel. Samples will be packaged by START/ERRS personnel and delivered to the laboratory by lab courier. The turnaround time for the sample data will be 5-7 days. The sampling results will be reviewed and validated by WESTON START if directed by the OSC.

5.0 Project Quality Objectives

5.1 Project Objectives

Sufficient data will be obtained from a representative number of samples to support implementation of leachate treatment system design. Representative leachate samples will be collected from landfill structures to assess the contaminant concentrations and water quality parameters in leachate. Collection of sufficient leachate samples will be dependent upon the available quantity of these liquids on the dates of the sampling events.

The following is a list of project objectives that apply to the sampling event:

- To assess air quality to determine the level of personal protective equipment that must be used by site workers
- To determine the appropriate treatment train to eliminate, reduce, or control risks to human health and the environment.
- To categorize waste material to support appropriate design elements and NPDES discharge requirements.

More information about the sampling procedures to support this is provided in Section 6.

5.2 Measurement and Performance Criteria

Generic measurement and performance criteria described in the *START III Generic QAPP* will be used. These criteria will ensure that data are sufficiently sensitive, precise, accurate, and

representative to support site decisions.

5.3 Data Quality Objectives

Data quality objectives address requirements that include when, where, and how to collect samples; the number of samples; and the limits on tolerable error rates. These steps should periodically be revisited as new information about a problem is learned.

START/ERRS Sample collection locations were determined based on review of historical information and the presence of existing leachate collection structures. The analytical data will be compared to:

Leachate

- Resource Conservation and Recovery Act Limits, as applicable
- NPDES limits for Frank and Poet Drain, Trenton Channel and Lake Erie
- MDEQ Water Quality Criteria

6.0 Sampling Design

- **Task 1 – Sample collection DSC 1A & 1B**
 - Static water level measurements and air monitoring readings will be collected from the leachate collection feature, as appropriate.
 - Up to a total of two liquid waste samples will be collected from the leachate collection feature to determine waste characterization and gather design information.

A static water level meter will be used to measure the liquid levels from the top of the leachate collection feature when appropriate. The total depth of the feature will also be recorded (liquid levels are expected to be as much as 25 – 30 feet deep). Air monitoring readings will be recorded at the feature head and in the breathing zone prior to collecting measurements.

Sample collection from a pump station at each fill area would be the most appropriate method for sample collection. The on site wastewater treatment operator will pump down each sump if sufficient room is available in the retention ponds for the leachate. START/ERRS will collect grab samples of liquid from the leachate collection feature. Either a bailer or submersible, variable speed centrifugal pump and associated tubing will be used to fill the appropriate laboratory-supplied sampling container. If sumps cannot be pumped fully out, sample collection will proceed as previously stated and when the last sump pump-down timeframe will be recorded.

- **Task 2 – Sample collection CWLF Upper**

- Static water level measurements and air monitoring readings will be collected from the leachate collection feature, as appropriate.
- Up to a total of four liquid waste samples will be collected from the leachate collection feature (previously identified as standpipes) to determine waste characteristics and further design information.

Landfill personnel will plan on pumping out the wells or they will be vacuumed out to serve as purging efforts for these wells within one day before sampling activities are to be conducted at this location.

A static water level meter will be used to measure the liquid levels from the top of the standpipes when appropriate. The total depth of the feature will also be recorded. Air monitoring readings will be recorded at the feature head and in the breathing zone prior to collecting measurements.

START/ERRS will collect grab samples from three of the six standpipes located at the western perimeter and one grab sample from an eastern perimeter standpipe.

Sample parameters, requirements for the sample container, volume, preservation, and QC samples are presented in Table 2: Sampling and Analysis Summary.

6.1 Sample Numbering System

All samples for analysis, including QC samples, will be given a unique sample number. The sample numbers will be recorded in the field logbook and on the COC paperwork.

WESTON START/ERRS will assign each sample its unique number. The sample number highlights the suspected contaminated area and location, and will be used for documentation purposes in field logbooks, as well as for presentation of the analytical data in memoranda and reports. The project samples will be identified using the following format:

Landfill Location Code

DSCG = Detroit Steel Company Gibraltar; CWLFU = County Wide Landfill; or CWLFL = County Wide Landfill Lower

Matrix Identification Code

LL = Liquid Leachate matrix

Date

Mm/dd/yy

Sample Location Code

A two to four alphabetical and/or numerical code to distinguish which feature the sample came from.

Examples of the sample identifications for the Site are as follows:

- DSCG-LL-111609-PS1A= DSC landfill, leachate liquid, sampled 11/16/09 from landfill Pump Station 1A. 1B would be used as appropriate
- CWLFL-LL-111609-EW= County Wide landfill Lower, leachate liquid, sampled 11/16/09, East Well. WW would be used as appropriate for west well.
- CWLFU-LL-111609-SP1= County Wide landfill Upper, leachate liquid, sampled 11/16/09, Stand Pipe 1 other standpipe numbers used appropriately.

6.2 Management of Investigation-Derived Wastes

For purposes of this FSP, investigation-derived wastes are defined as any byproduct of the field activities that is suspected or known to be contaminated with hazardous substances. The performance of field activities will produce waste products, such as spent sampling supplies (*e.g.*, tubing, etc.), and expendable Personal Protective Equipment (PPE). START/ERRS may also generate decontamination water.

Disposable sampling supplies and PPE will be containerized in trash bags and to remain on-site pending the receipt of sample laboratory analytical results. It is anticipated decontamination water will be placed in the existing treatment system retention ponds.

7.0 Sampling Procedures

7.1 Sampling Standard Operating Procedures

The following Standard Operating Procedures (SOPs) will be used during the site evaluation:

List Sampling SOPs that will be used (Refer to START III Generic QAPP Appendices).

1. SOP 204 – Water Level
2. SOP 2012 – Sampling Equipment Decontamination

U.S. EPA Method 1669 will be followed for collection of the low level mercury fraction of leachate samples.

7.2 Decontamination Procedures

General decontamination procedures are described in Section B.2 of the *START III Generic QAPP*. All non-disposable equipment (*i.e.* interface water level meter) will be decontaminated prior to demobilizing from the Site.

8.0 Sample Handling, Tracking, and Custody Procedures

All samples will be identified, handled, shipped, tracked, and maintained under COC, in accordance

with the *START III Generic QAPP*.

9.0 Field Analytical Methods and Procedures

9.1 Field Analytical Methods and Standard Operating Procedures

The following procedures and methods will be used:

Field screening of the headspace at the top of the standpipes and other landfill leachate features will be conducted with a 5-gas air monitor. Air monitoring readings will be recorded in the site log book. Water level measurements will be collected from standpipes and any other applicable landfill leachate features with a standard water level meter and measurements will be recorded in the log book.

9.2 Field Testing Laboratory

A field testing laboratory will not be used during the site assessment.

9.3 Screening/Confirmatory Analyses

Screening/Confirmatory Analyses will not be used during the site assessment.

10.0 Fixed Laboratory Analytical Methods and Procedures

Analytical methods and procedures are referenced in Table 2 – Sampling and Analysis Summary.

11.0 Quality Control Activities

Trace Analytical Labs, Inc
2241 Black Creek RD
Muskegon, MI, 49444
Contact: John Mink
Office: (231)773-5998
Fax: (231)-773-6537

11.1 Field Quality Control

The number of QC samples collected for each analytical parameter and concentration level are listed in Table 2: Sampling and Analysis Summary. The QC sample determination and frequency is in general accordance with the *START III Generic QAPP*, Table 4. However, the samples to be collected are for pre-design considerations and not to determine the nature and extent of contamination. Therefore, some QC samples were not deemed necessary.

11.2 Analytical Quality Control

QC for analytical procedures will be performed at the general frequency described in the *START III*

Generic QAPP, Tables 5 and 6. In addition, method-specific QC requirements will be used to ensure data quality.

11.3 Performance Evaluation Samples

Performance evaluation samples will not be used in this sampling event.

12.0 Documentation, Records, and Data Management

Documentation, record keeping, and data management activities will be conducted in accordance with the *START III Generic QAPP*, Section B.10.

13.0 Quality Assurance Assessment and Corrective Actions

Field activities are anticipated to require two days for completion; no-long-term project field audit will be completed at this time.

14.0 Reports to Management

Reports to management will be written and distributed in accordance with the *START III Generic QAPP*, Section C.

15.0 Steps 1, 2 and 3: Data Review Requirements and Procedures

Step 1: Data collection activities, including sample collection and data generation, will be verified in accordance with the *START III Generic QAPP*, Section D.

Step 2: Data will be validated by WESTON START, if necessary.

Step 3: Data will be reviewed for usability in accordance with the *START III Generic QAPP*, Section D, if necessary.

TABLES

Table 1 **FSP Revision Form**

Site: Detroit Steel Company Gibraltar

OSC: Brian Kelly

TDD: S05-0001-0910-016

Date	Revision Number	Proposed Change to FSP/QAPP	Reason for Change of Scope/Procedures	FSP Section Superseded	Requested By	Approved By

Table 2
Sampling and Analysis Summary

Site: Detroit Steel Company Gibraltar

OSC: Brian Kelly

TDD: S05-0001-0910-016

Matrix	Analytical Parameter	Analytical Method	Containers (Numbers, Size, and Type)	Preservation Requirements	Number of Sampling Locations	Number of Field Duplicates	Number of MS/ MSDs ²	Number of Blanks (Trip, Field, Equip. Rinsate) ¹	Total Number of Samples to Lab ³	Holding Time
Leachate	Total Metals*	EPA 200.7/200.8	250mL plastic	Nitric Acid (HN03)	9	0	0	0	9	180 days
Leachate	Dissolved Metals	EPA 200.7/200.8/	1000ml plastic	Cool to 4°C	9	0	0	0	9	1 Day to Filter 180 days analytical
Leachate	Total and Dissolved LL Mercury	EPA 1631E	250ml glass (double bagged)	Cool to 4°C	9	1	0	4 (1 trip and 1 equipment rinse for each day of sampling)	14	1 Day to Filter 28 days for analysis
Leachate	Full List SVOC's	625	1 liter amber	Cool to 4°C	9	0	0	0	9	7 days to extraction/ 40 days from ext. to analysis
Leachate	Full List VOCs	624	2 40ml Glass Vials	Hydrochloric Acid (HCL)	9	0	0	2	11	14 Days
Leachate	Pest/PCB	608	1 liter amber	Cool to 4°C	9	0	0	0	9	7 days to extraction/ 40 days from ext.

Table 2
Sampling and Analysis Summary
(Cont'd)

Site: Detroit Steel Company Gibraltar

OSC: Brian Kelly

TDD: S05-0001-0910-016

Matrix	Analytical Parameter	Analytical Method	Containers (Numbers, Size, and Type)	Preservation Requirements	Number of Sampling Locations	Number of Field Duplicates	Number of MS/ MSDs ²	Number of Blanks (Trip, Field, Equip. Rinsate) ¹	Total Number of Samples to Lab ³	Holding Time
										to analysis
Leachate	Ammonia as nitrogen	EPA 350.1 Rev 2.0	250 mL plastic	Sulfuric Acid (H ₂ SO ₄)	9	0	0	0	9	28 Days
Leachate	Biological Oxygen Demand (BOD)	SM 5210 B-01	1000 mL plastic	Cool to 4°C	9	0	0	0	9	2 Days
Leachate	Chemical Oxygen Demand (COD)	EPA 410.4 Rev2.0	250 ml plastic	Sulfuric Acid (H ₂ SO ₄) Cool to 4°C	9	0	0	0	9	28 Days
Leachate	Total Suspended Solids (TSS)	SM 2540 D-97	1000mL plastic	Cool to 4°C	9	0	0	0	9	7 Days
Leachate	Total Solids (TS)	SM 2540 B-97	1000mL plastic	Cool to 4°C	9	0	0	0	9	7 Days
Leachate	Total Dissolved Solids (TDS By calculation)	SM 2540 B-97	1000mL plastic	Cool to 4°C	9	0	0	0	9	7 Days

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Table 2
Sampling and Analysis Summary
(Cont'd)

Site: Detroit Steel Company Gibraltar

OSC: Brian Kelly

TDD: S05-0001-0910-016

Matrix	Analytical Parameter	Analytical Method	Containers (Numbers, Size, and Type)	Preservation Requirements	Number of Sampling Locations	Number of Field Duplicates	Number of MS/ MSDs ²	Number of Blanks (Trip, Field, Equip. Rinsate) ¹	Total Number of Samples to Lab ³	Holding Time
Leachate	Oil & Grease (O & G)	EPA 1664A	1 liter amber	Hydrochloric Acid(HCL) Cool to 4°C	9	0	0	0	9	28 Days
Leachate	Cyanide	EPA 335.4 Rev 1.0	125 mL plastic	Sulfuric Acid (H ₂ SO ₄) Cool to 4°C	9	0	0	0	9	14 Days
Leachate	Bicarbonate	SM 2320 B-97	1000mL plastic	Cool to 4°C	9	0	0	0	9	14 Days
Leachate	Carbonate	SM 2320 B-97	1000mL plastic	Cool to 4°C	9	0	0	0	9	14 Days
Leachate	Total Organic Carbon (TOC)	SM 5310 D-00	250 mL plastic	Sulfuric Acid (H ₂ SO ₄) Cool to 4°C	9	0	0	0	9	28 Days
Leachate	Sulfates	EPA 300.0 Rev 2.1	1000mL plastic	Cool to 4°C	9	0	0	0	9	28 Day
Leachate	Chloride	EPA 300.0 Rev 2.1	1000mL plastic	Cool to 4°C	9	0	0	0	9	28 Days

Table 2
Sampling and Analysis Summary
(Cont'd)

Site: Detroit Steel Company Gibraltar

OSC: Brian Kelly

TDD: S05-0001-0910-016

Matrix	Analytical Parameter	Analytical Method	Containers (Numbers, Size, and Type)	Preservation Requirements	Number of Sampling Locations	Number of Field Duplicates	Number of MS/ MSDs ²	Number of Blanks (Trip, Field, Equip. Rinsate) ¹	Total Number of Samples to Lab ³	Holding Time
Leachate	Hardness	SM 2340 B			9	0	0	0	9	180 Days
Leachate	Fluoride	EPA 300.0 Rev 2.1	1000mL plastic	Cool to 4°C	9	0	0	0	9	28 Days
Leachate	Nitrate /Nitrite	EPA 300.0 Rev 2.1	1000mL plastic	Cool to 4°C	9	0	0	0	9	2 Days
Leachate	Acute Toxicity (Both species)	EPA-821-R-02-012	1 gallon plastic	Hydrochloric Acid (HCL) Cool to 4°C	9	0	0	0	9	1.5 Days

Notes:

* Hexavalent Chromium by SM 3500-Cr B-01 has a 1 day hold

* Ferrous Iron by SM 3500 Fe-D has a 1 day hold

FIGURES

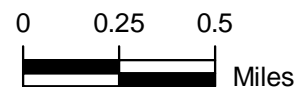


Figure 3-1



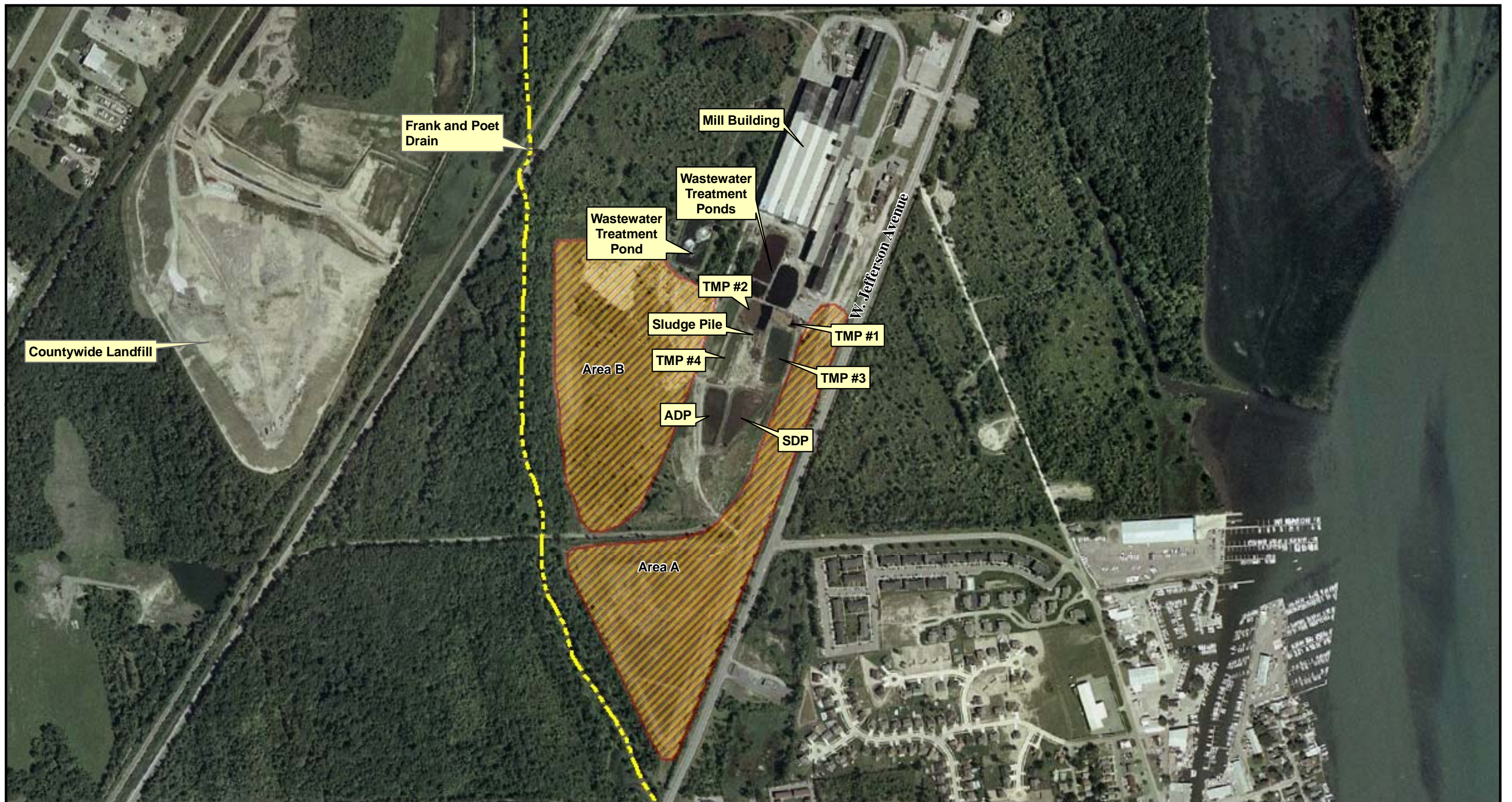
Prepared for:
U.S. EPA REGION V
Contract No: EP-S5-06-04

TDD No.: S05-0002-0706-009
DCN: 808-4H-AFEO



Prepared by:
WESTON SOLUTIONS, INC.
7800 W. Outer Drive, Suite 200
Detroit, MI



SITE LOCATION MAP
DETROIT STEEL CO. SITE
GIBRALTAR, WAYNE CO., MI
DECEMBER 2007
Scale: 1" = 0.5 Miles



Source of Imagery: ESRI I3 Imagery Prime World 2007-01-15

Figure 3-2

Figure Key/Notes

-  Estimated Extent of 1A/1B
-  Approximate Drain Location
- TMP - Tandem Mill Pond
- ADP - Acid Dosing Pond
- SDP - Sludge Drying Pond



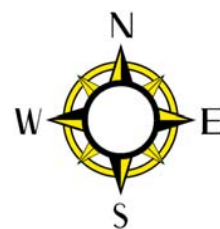
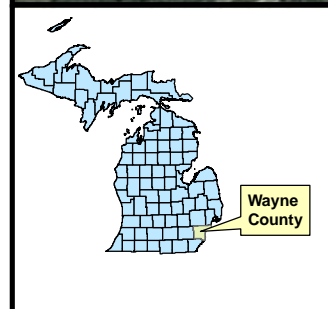
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Prepared by:
WESTON SOLUTIONS, INC.
7800 W. Outer Drive, Suite 200
Detroit, MI 48235

SITE LAYOUT MAP
DETROIT STEEL CO. SITE
GIBRALTAR, WAYNE CO., MI
NOVEMBER 2009
Scale: 1" = 600'



0 300 600
Feet

ATTACHMENTS



GROUNDWATER WELL SAMPLING

SOP#: 2007
DATE: 01/26/95
REV. #: 0.0

1.0 SCOPE AND APPLICATION

The objective of this standard operating procedure (SOP) is to provide general reference information on sampling of ground water wells. This guideline is primarily concerned with the collection of water samples from the saturated zone of the subsurface. Every effort must be made to ensure that the sample is representative of the particular zone of water being sampled. These procedures are designed to be used in conjunction with analyses for the most common types of ground water contaminants (e.g., volatile and semi-volatile organic compounds, pesticides, metals, biological parameters).

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent upon site conditions, equipment limitations or limitations imposed by the procedure. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. Environmental Protection Agency (EPA) endorsement or recommendation for use.

2.0 METHOD SUMMARY

In order to obtain a representative groundwater sample for chemical analysis it is important to remove stagnant water in the well casing and the water immediately adjacent to the well before collection of the sample. This may be achieved with one of a number of instruments. The most common of these are the bailer, submersible pump, non-contact gas bladder pump, inertia pump and suction pump. At a minimum, three well volumes should be purged, if possible. Equipment must be decontaminated prior to use and between wells. Once purging is completed and the correct laboratory-cleaned sample containers have been prepared, sampling may proceed. Sampling may be conducted with any of the above instruments,

and need not be the same as the device used for purging. Care should be taken when choosing the sampling device as some will affect the integrity of the sample. Sampling should occur in a progression from the least to most contaminated well, if this information is known.

The growing concern over the past several years over low levels of volatile organic compounds in water supplies has led to the development of highly sophisticated analytical methods that can provide detection limits at part per trillion levels. While the laboratory methods are extremely sensitive, well controlled and quality assured, they cannot compensate for a poorly collected sample. The collection of a sample should be as sensitive, highly developed and quality assured as the analytical procedures.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

The type of analysis for which a sample is being collected determines the type of bottle, preservative, holding time, and filtering requirements. Samples should be collected directly from the sampling device into appropriate laboratory cleaned containers. Check that a Teflon liner is present in the cap, if required. Attach a sample identification label. Complete a field data sheet, a chain of custody form, and record all pertinent data in the site logbook.

Samples shall be appropriately preserved, labelled, logged, and placed in a cooler to be maintained at 4EC. Samples must be shipped well before the holding time is up and ideally should be shipped within 24 hours of sample collection. It is imperative that samples be shipped or delivered daily to the analytical laboratory in order to maximize the time available for the laboratory to perform the analyses. The bottles should be shipped with adequate packing and cooling to ensure that they arrive intact.

Sample retrieval systems suitable for the valid collection of volatile organic samples are: positive displacement bladder pumps, gear driven submersible pumps, syringe samplers and bailers (Barcelona, 1984; Nielsen, 1985). Field conditions and other constraints will limit the choice of appropriate systems. The focus of concern must remain to provide a valid sample for analysis, one which has been subjected to the least amount of turbulence possible.

Treatment of the sample with sodium thiosulfate preservative is required only if there is residual chlorine in the water that could cause free radical chlorination and change the identity of the original contaminants. It should not be used if there is no chlorine in the water.

Holding time for volatiles analysis is seven days. It is imperative that the sample be shipped or delivered daily to the analytical laboratory. The bottles must be shipped on their sides to aid in maintaining the airtight seal during shipment, with adequate packing and cooling to ensure that they arrive intact.

For collection of volatile organic samples, refer to the work plan to ensure that 40 mL glass sample vials with Teflon lined septa are ordered and in sufficient numbers. Check sampling supplies; field kit for chlorine, preservatives, Parafilm, foam sleeves and coolers. Due to the extreme trace levels at which volatile organics are detectable, cross contamination and introduction of contaminants must be avoided. Trip blanks are incorporated into the shipment package to provide a check against cross contamination.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

4.1 General

The primary goal in performing ground water sampling is to obtain a representative sample of the ground water body. Analysis can be compromised by field personnel in two primary ways: (1) taking an unrepresentative sample, or (2) by incorrect handling of the sample. There are numerous ways of introducing foreign contaminants into a sample, and these must be avoided by following strict sampling procedures and utilizing trained field personnel.

4.2 Purging

In a nonpumping well, there will be little or no vertical mixing of the water, and stratification will occur. The well water in the screened section will mix with the ground water due to normal flow patterns, but the well water above the screened section will remain isolated, become stagnant, and may lack the contaminants representative of the ground water. Persons sampling should realize that stagnant water may contain foreign material inadvertently or deliberately introduced from the surface, resulting in an unrepresentative sample. To safeguard against collecting nonrepresentative stagnant water, the following guidelines and techniques should be adhered to during sampling:

1. As a general rule, all monitor wells should be pumped or bailed prior to sampling. Purge water should be containerized on site or handled as specified in the site specific project plan. Evacuation of a minimum of one volume of water in the well casing, and preferably three to five volumes, is recommended for a representative sample. In a high-yielding ground water formation and where there is no stagnant water in the well above the screened section, evacuation prior to sample withdrawal is not as critical. However, in all cases where the monitoring data is to be used for enforcement actions, evacuation is recommended.
2. When purging with a pump (not a bailer), the pump should be set at the screened interval, or if the well is an open-rock well, it should be set at the same depth the sample will be collected. When sampling a screened well, the sample should also be collected from the same depth the pump was set at.
3. The well should be sampled as soon as possible after purging.
4. Analytical parameters typically dictate whether the sample should be collected through the purging device, or through a separate sampling instrument.
5. For wells that can be pumped or bailed to dryness with the equipment being used, the well should be evacuated and allowed to

recover prior to collecting a sample. If the recovery rate is fairly rapid and time allows, evacuation of more than one volume of water is preferred. If recovery is slow, sample the well upon recovery after one evacuation.

6. A non-representative sample can also result from excessive pre-pumping of the monitoring well. Stratification of the leachate concentration in the ground water formation may occur, or heavier-than-water compounds may sink to the lower portions of the aquifer. Excessive pumping can dilute or increase the contaminant concentrations from what is representative of the sampling point of interest.

4.3 Materials

Materials of construction for samplers and evacuation equipment (bladders, pump, bailers, tubing, etc.) should be limited to stainless steel, Teflon[®], and glass in areas where concentrations are expected to be at or near the detection limit. The tendency of organics to leach into and out of many materials make the selection of materials critical for trace analyses. The use of plastics, such as PVC or polyethylene, should be avoided when analyzing for organics. However, PVC may be used for evacuation equipment as it will not come in contact with the sample, and in highly contaminated wells, disposable equipment (i.e., polypropylene bailers) may be appropriate to avoid cross-contamination.

Materials of construction (bladders/ pumps, bailers, tubing, etc.) suitable for collecting and handling Volatile Organic Samples should be limited to stainless steel, Teflon and glass in areas which detection limit range concentrations are expected. The tendency of organics to leach into and out of many materials, make the selection of materials critical for these trace analyses. The use of plastics, e.g., PVC etc., should be avoided. There are numerous ways of introducing foreign contaminants into a sample, and these must be avoided by following strict sampling procedures and utilization of trained personnel.

4.4 Advantages/Disadvantages of Certain Equipment

4.4.1 Bailers

Advantages

- C Only practical limitations on size and materials
- C No power source needed
- C Portable
- C Inexpensive, so it can be dedicated and hung in a well, thereby reducing the chances of cross contamination
- C Minimal outgassing of volatile organics while sample is in bailer
- C Readily available
- C Removes stagnant water first
- C Rapid, simple method for removing small volumes of purge water

Disadvantages

- C Time-consuming to flush a large well of stagnant water
- C Transfer of sample may cause aeration
- C Stoppers at the bottom of the bailer usually leak thus the bailer must be brought to the surface rapidly
- C If the bailer is allowed to hit the bottom of the well boring, gravel can displace the ball valve not allowing the bailer to hold water

4.4.2 Submersible Pumps

Advantages

- C Portable and can be transported to several wells
- C Depending upon the size of the pump and the pumping depths, relatively high pumping rates are possible
- C Generally very reliable and does not require priming

Disadvantages

- C Potential for effects on analysis of trace organics
- C Heavy and cumbersome to deal with, particularly in deeper wells
- C Expensive
- C Power source needed
- C Sediment in water may cause problems with the pumps
- C Impractical in low yielding or shallow wells

4.4.3 Non-Contact Gas Bladder Pumps

Advantages

- C Maintains integrity of sample
- C Easy to use
- C Can sample from discrete locations within the monitor well

Disadvantages

- C Difficulty in cleaning, though dedicated tubing and bladder may be used
- C Only useful to about 100 feet
- C Supply of gas for operation, gas bottles and/or compressors are often difficult to obtain and are cumbersome
- C Relatively low pumping rates
- C Requires air compressor or pressurized gas source and control box

4.4.4 Suction Pumps

Advantages

- C Portable, inexpensive, and readily available

Disadvantages

- C Restricted to areas with water levels within 20 to 25 feet of the ground surface
- C Vacuum can cause loss of dissolved gasses and volatile organics
- C Pump must be primed and vacuum is often difficult to maintain during initial stages of pumping

4.4.5 Inertia Pumps

Advantages

- C Portable, inexpensive, and readily available
- C Offers a rapid method for purging relatively shallow wells

Disadvantages

- C Restricted to areas with water levels within 70 feet of the ground surface
- C May be time consuming to purge wells with these manual pumps
- C Labor intensive
- C WaTerra pumps are only effective in 2-inch diameter wells

5.0 EQUIPMENT APPARATUS

5.1 Equipment Checklist

5.1.1 General

- C Water level indicator
 - electric sounder
 - steel tape
 - transducer
 - reflection sounder
 - airline
- C Depth sounder
- C Appropriate keys for well cap locks
- C Steel brush
- C HNU or OVA (whichever is most appropriate)
- C Logbook
- C Calculator
- C Field data sheets and samples labels

- C Chain of custody records and seals
- C Sample containers
- C Engineer's rule
- C Sharp knife (locking blade)
- C Tool box (to include at least: screwdrivers, pliers, hacksaw, hammer, flashlight, adjustable wrench)
- C Leather work gloves
- C Appropriate Health & Safety gear
- C 5-gallon pail
- C Plastic sheeting
- C Shipping containers
- C Packing materials
- C Bolt cutters
- C Ziploc plastic bags
- C Containers for evacuation liquids
- C Decontamination solutions
- C Tap water
- C Non phosphate soap
- C Several brushes
- C Pails or tubs
- C Aluminum foil
- C Garden sprayer
- C Preservatives
- C Distilled or deionized water
- C Fire extinguisher (if using a generator for your power source)

5.1.2 Bailers

- C Clean, decontaminated bailers of appropriate size and construction material
- C Nylon line, enough to dedicate to each well
- C Teflon coated bailer wire
- C Sharp knife
- C Aluminum foil (to wrap clean bailers)
- C Five gallon bucket

5.1.3 Submersible Pump

- C Pump(s)
- C Generator (110, 120, or 240 volt) or 12 volt battery if inaccessible to field vehicle - amp meter is useful
- C 1" black PVC coil tubing - enough to dedicate to each well
- C Hose clamps
- C Safety cable
- C Tool box supplement
 - pipe wrenches

- wire strippers
- electrical tape
- heat shrink
- hose connectors
- Teflon tape

- C Winch, pulley or hoist
- C Gasoline for generator/gas can
- C Flow meter with gate valve
- C 1" nipples and various plumbing (i.e., pipe connectors)
- C Control box (if necessary)

5.1.4 Non-Gas Contact Bladder Pump

- C Non-gas contact bladder pump
- C Compressor or nitrogen gas tank
- C Batteries and charger
- C Teflon tubing - enough to dedicate to each well
- C Swagelock fitting
- C Toolbox supplements - same as submersible pump
- C Control box (if necessary)

5.1.5 Suction Pump

- C Pump
- C 1" black PVC coil tubing - enough to dedicate to each well
- C Gasoline - if required
- C Toolbox
- C Plumbing fittings
- C Flow meter with gate valve

5.1.6 Inertia Pump

- C Pump assembly (WaTerra pump, piston pump)
- C Five gallon bucket

6.0 REAGENTS

Reagents may be utilized for preservation of samples and for decontamination of sampling equipment. The preservatives required are specified by the analysis to be performed. Decontamination solutions are specified in ERT SOP #2006, Sampling Equipment Decontamination.

7.0 PROCEDURE

7.1 Preparation

1. Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies needed (i.e., diameter and depth of wells to be sampled).
2. Obtain necessary sampling and monitoring equipment, appropriate to type of contaminant being investigated. For collection of volatile organic samples, refer to the work plan to ensure that 40 mL glass sample vials with Teflon lined septa are ordered and in sufficient numbers. Check sampling supplies; field kit for chlorine, preservatives, Parafilm, foam sleeves and coolers. Due to extreme trace levels at which volatile organics are detectable, cross contamination and introduction of contaminants must be avoided. Trip blanks are incorporated into the shipment package to provide a check against cross contamination.
3. Decontaminate or preclean equipment, and ensure that it is in working order.
4. Prepare scheduling and coordinate with staff, clients, and regulatory agency, if appropriate.
5. Perform a general site survey prior to site entry in accordance with the site specific Health and Safety Plan.
6. Identify and mark all sampling locations.

7.2 Field Preparation

1. Start at the least contaminated well, if known.
2. Lay plastic sheeting around the well to minimize likelihood of contamination of equipment from soil adjacent to the well.
3. Remove locking well cap, note location, time of day, and date in field notebook or appropriate log form.
4. Remove well casing cap.

5. Screen headspace of well with an appropriate monitoring instrument to determine the presence of volatile organic compounds and record in site logbook.
6. Lower water level measuring device or equivalent (i.e., permanently installed transducers or airline) into well until water surface is encountered.
7. Measure distance from water surface to reference measuring point on well casing or protective barrier post and record in site logbook. Alternatively, if no reference point, note that water level measurement is from top of steel casing, top of PVC riser pipe, from ground surface, or some other position on the well head.

If floating organics are of concern, this can be determined by measuring the water level with an oil/water interface probe which measures floating organics.
8. Measure total depth of well (at least twice to confirm measurement) and record in site logbook or on field data sheet.
9. Calculate the volume of water in the well and the volume to be purged using the calculations in Section 8.0.
10. Select the appropriate purging and sampling equipment.
11. If residual chlorine is suspected, use the Hach Field Test Kit for chlorine to determine if there is residual chlorine in the water to be sampled. If there is, treat the sample vial with a crystal of sodium thiosulfate prior to sample collection.

7.3 Purging

The amount of flushing a well receives prior to sample collection depends on the intent of the monitoring program as well as the hydrogeologic conditions. Programs where overall quality determination of water resources are involved may require long pumping periods to obtain a sample that is representative of a large volume of that aquifer. The pumped volume can be determined prior to sampling so that the sample is

a collected after a known volume of the water is evacuated from the aquifer, or the well can be pumped until the stabilization of parameters such as temperature, electrical conductance, pH, or turbidity has occurred.

However, monitoring for defining a contaminant plume requires a representative sample of a small volume of the aquifer. These circumstances require that the well be pumped enough to remove the stagnant water but not enough to induce flow from other areas. Generally, three well volumes are considered effective, or calculations can be made to determine, on the basis of the aquifer parameters and well dimensions, the appropriate volume to remove prior to sampling.

During purging, water level measurements may be taken regularly at 15-30 second intervals. This data may be used to compute aquifer transmissivity and other hydraulic characteristics. The following well evacuation devices are most commonly used. Other evacuation devices are available, but have been omitted in this discussion due to their limited use.

7.3.1 Bailers

Bailers are the simplest purging device used and have many advantages. They generally consist of a rigid length of tube, usually with a ball check-valve at the bottom. A line is used to lower the bailer into the well and retrieve a volume of water. The three most common types of bailer are PVC, Teflon, and stainless steel.

This manual method of purging is best suited to shallow or narrow diameter wells. For deep, larger diameter wells which require evacuation of large volumes of water, other mechanical devices may be more appropriate.

7.3.1.1 Operation

Equipment needed will include a clean decontaminated bailer, Teflon or nylon line, a sharp knife, and plastic sheeting.

1. Determine the volume of water to be purged as described in 8.0, calculations.
2. Lay plastic sheeting around the well to prevent contamination of the bailer line with

foreign materials.

3. Attach the line to the bailer and slowly lower until the bailer is completely submerged, being careful not to drop the bailer to the water, causing turbulence and the possible loss of volatile organic contaminants.
4. Pull bailer out ensuring that the line either falls onto a clean area of plastic sheeting or never touches the ground.
5. Empty the bailer into a pail until full to determine the number of bails necessary to achieve the required purge volume.
6. Thereafter, pour the water into a container and dispose of purge waters as specified in the site specific sampling plan.

7.3.2 Submersible Pumps

The use of submersible pumps for sample collection is permissible provided they are constructed of suitably noncontaminating materials. The chief drawback, however, is the difficulty avoiding cross-contamination between wells. Although some units can be disassembled easily to allow surfaces contacted by contaminants to be cleaned, field decontamination may be difficult and require solvents that can affect sample analysis. The use of submersible pumps in multiple well-sampling programs, therefore, should be carefully considered against other sampling mechanisms (bailers, bladder pumps). In most cases, a sample can be collected by bailer after purging with a submersible pump, however, submersible pumps may be the only practical sampling device for extremely deep wells (greater than 300 feet of water). Under those conditions, dedicated pump systems should be installed to eliminate the potential for cross-contamination of well samples.

Submersible pumps generally use one of two types of power supplies, either electric or compressed gas or air. Electric powered pumps can run off a 12 volt DC rechargeable battery, or a 110 or 220 volt AC power supply. Those units powered by compressed air normally use a small electric or gas-powered air compressor. They may also utilize compressed gas (i.e., nitrogen) from bottles. Different size pumps are available for different depth or diameter monitoring wells.

7.3.2.1 Operation

1. Determine the volume of water to be purged as described in 8.0 Calculations.
2. Lay plastic sheeting around the well to prevent contamination of pumps, hoses or lines with foreign materials.
3. Assemble pump, hoses and safety cable, and lower the pump into the well. Make sure the pump is deep enough so all the water is not evacuated. (Running the pump without water may cause damage.)
4. Attach flow meter to the outlet hose to measure the volume of water purged.
5. Use a ground fault circuit interrupter (GFCI) or ground the generator to avoid possible electric shock.
6. Attach power supply, and purge the well until the specified volume of water has been evacuated (or until field parameters, such as temperature, pH, conductivity, etc, have stabilized). Do not allow the pump to run dry. If the pumping rate exceeds the well recharge rate, lower the pump further into the well, and continue pumping.
7. Collect and dispose of purge waters as specified in the site specific sampling plan.

7.3.3 Non-Contact Gas Bladder Pumps

For this procedure, an all stainless-steel and Teflon Middleburg-squeeze bladder pump (e.g., IEA, TIMCO, Well Wizard, Geoguard, and others) is used to provide the least amount of material interference to the sample (Barcelona, 1985). Water comes into contact with the inside of the bladder (Teflon) and the sample tubing, also Teflon, that may be dedicated to each well. Some wells may have permanently installed bladder pumps, (i.e., Well Wizard, Geoguard), that will be used to sample for all parameters.

7.3.3.1 Operation

1. Assemble Teflon tubing, pump and charged control box.
2. Procedure for purging with a bladder pump is

the same as for a submersible pump (Section 7.3.2.1).

3. Be sure to adjust flow rate to prevent violent jolting of the hose as sample is drawn in.

7.3.4 Suction Pumps

There are many different types of suction pumps. They include: centrifugal, peristaltic and diaphragm. Diaphragm pumps can be used for well evacuation at a fast pumping rate and sampling at a low pumping rate. The peristaltic pump is a low volume pump that uses rollers to squeeze the flexible tubing thereby creating suction. This tubing can be dedicated to a well to prevent cross contamination. Peristaltic pumps, however, require a power source.

7.3.4.1 Operation

1. Assembly of the pump, tubing, and power source if necessary.
2. Procedure for purging with a suction pump is exactly the same as for a submersible pump (Section 7.3.2.1).

7.3.5 Inertia Pumps

Inertia pumps such as the WaTerra pump and piston pump, are manually operated. They are most appropriate to use when wells are too deep to bail by hand, or too shallow or narrow (or inaccessible) to warrant an automatic (submersible, etc.) pump. These pumps are made of plastic and may be either decontaminated or discarded.

7.3.5.1 Operation

1. Determine the volume of water to be purged as described in 8.0, Calculations.
2. Lay plastic sheeting around the well to prevent contamination of pumps or hoses with foreign materials.
3. Assemble pump and lower to the appropriate depth in the well.
4. Begin pumping manually, discharging water into a 5 gallon bucket (or other graduated vessel). Purge until specified volume of water has been evacuated (or until field parameters such as temperature, pH,

conductivity, etc. have stabilized).

5. Collect and dispose of purge waters as specified in the site specific project plan.

7.4 Sampling

Sample withdrawal methods require the use of pumps, compressed air, bailers, and samplers. Ideally, purging and sample withdrawal equipment should be completely inert, economical to manufacture, easily cleaned, sterilized, reusable, able to operate at remote sites in the absence of power resources, and capable of delivering variable rates for sample collection.

There are several factors to take into consideration when choosing a sampling device. Care should be taken when reviewing the advantages or disadvantages of any one device. It may be appropriate to use a different device to sample than that which was used to purge. The most common example of this is the use of a submersible pump to purge and a bailer to sample.

7.4.1 Bailers

The positive-displacement volatile sampling bailer is perhaps the most appropriate for collection of water samples for volatile analysis. Other bailer types (messenger, bottom fill, etc.) are less desirable, but may be mandated by cost and site conditions.

7.4.1.1 Operation

1. Surround the monitor well with clean plastic sheeting. If using the GPI bailer, insert a vial into the claim and assemble the unit.
2. Attach a line to a clean decontaminated bailer.
3. Lower the bailer slowly and gently into the well, taking care not to shake the casing sides or to splash the bailer into the water. Stop lowering at a point adjacent to the screen.
4. Allow bailer to fill and then slowly and gently retrieve the bailer from the well avoiding contact with the casing, so as not to knock flakes of rust or other foreign materials into the bailer. If using the GPI bailer for collecting volatile organic samples,

once at the surface, remove the bailer from the cable. Carefully open the GPI bailer unit and remove the vial. Begin slowly pouring from the bailer, and collect the duplicate samples from the midstream sample.

5. Remove the cap from the sample container and place it on the plastic sheet or in a location where it won't become contaminated. See Section 7.7 for special considerations on VOA samples.
6. Begin slowly pouring from the bailer.
7. Filter and preserve samples as required by sampling plan.
8. Cap the sample container tightly and place prelabeled sample container in a carrier.
9. Replace the well cap.
10. Log all samples in the site logbook and on field data sheets and label all samples.
11. Package samples and complete necessary paperwork.
12. Transport sample to decontamination zone for preparation for transport to analytical laboratory.

7.4.2 Submersible Pumps

Although it is recommended that samples not be collected with a submersible pump due to the reasons stated in Section 4.4.2, there are some situations where they may be used.

7.4.2.1 Operation

1. Allow the monitor well to recharge after purging, keeping the pump just above screened section.
2. Attach gate valve to hose (if not already fitted), and reduce flow of water to a manageable sampling rate.
3. Assemble the appropriate bottles.
4. If no gate valve is available, run the water

- down the side of a clean jar and fill the sample bottles from the jar.
5. Cap the sample container tightly and place prelabeled sample container in a carrier.
 6. Replace the well cap.
 7. Log all samples in the site logbook and on the field data sheets and label all samples.
 8. Package samples and complete necessary paperwork.
 9. Transport sample to decontamination zone for preparation for transport to the analytical laboratory.
 10. Upon completion, remove pump and assembly and fully decontaminate prior to setting into the next sample well. Dedicate the tubing to the hole.

7.4.3 Non-Contact Gas Bladder Pumps

The use of a non-contact gas positive displacement bladder pump is often mandated by the use of dedicated pumps installed in wells. These pumps are also suitable for shallow (less than 100 feet) wells. They are somewhat difficult to clean, but may be used with dedicated sample tubing to avoid cleaning. These pumps require a power supply and a compressed gas supply (or compressor). They may be operated at variable flow and pressure rates making them ideal for both purging and sampling.

Barcelona (1984) and Nielsen (1985) report that the non-contact gas positive displacement pumps cause the least amount of alteration in sample integrity as compared to other sample retrieval methods.

7.4.3.1 Operation

1. Allow well to recharge after purging.
2. Assemble the appropriate bottles.
3. Turn pump on, increase the cycle time and reduce the pressure to the minimum that will allow the sample to come to the surface.
4. Cap the sample container tightly and place

prelabeled sample container in a carrier.

5. Replace the well cap.
6. Log all samples in the site logbook and on field data sheets and label all samples.
7. Package samples and complete necessary paperwork.
8. Transport sample to decontamination zone for preparation for transport to analytical laboratory.
9. On completion, remove the tubing from the well and either replace the Teflon tubing and bladder with new dedicated tubing and bladder or rigorously decontaminate the existing materials.
10. Nonfiltered samples shall be collected directly from the outlet tubing into the sample bottle.
11. For filtered samples, connect the pump outlet tubing directly to the filter unit. The pump pressure should remain decreased so that the pressure build up on the filter does not blow out the pump bladder or displace the filter. For the Geotech barrel filter, no actual connections are necessary so this is not a concern.

7.4.4 Suction Pumps

In view of the limitations of these type pumps, they are not recommended for sampling purposes.

7.4.5 Inertia Pumps

Inertia pumps may be used to collect samples. It is more common, however, to purge with these pumps and sample with a bailer (Section 7.4.1).

7.4.5.1 Operation

1. Following well evacuation, allow the well to recharge.
2. Assemble the appropriate bottles.
3. Since these pumps are manually operated,

the flow rate may be regulated by the sampler. The sample may be discharged from the pump outlet directly into the appropriate sample container.

4. Cap the sample container tightly and place prelabeled sample container in a carrier.
5. Replace the well cap.
6. Log all samples in the site logbook and on field data sheets and label all samples.
7. Package samples and complete necessary paperwork.
8. Transport sample to decontamination zone for preparation for transport to the analytical laboratory.
9. Upon completion, remove pump and decontaminate or discard, as appropriate.

7.4.6. Sample Retrieval - Syringe

A limited number of commercial syringe type samplers are available, (IEA, TIMCO, etc.) some are homemade devices. These devices are claimed to provide good quality samples for volatile analysis, but are severely limited in sample volume and are specific to sampling for volatiles. Essentially, they operated with an evacuated chamber that is lowered down the well, and allowed to fill with the pressure of the water. The entire mechanism is then brought to the surface with the sample. The sample may then be transferred to a sample vial, or the entire unit may be sent as the sample container.

1. Evacuate the syringe if necessary, and lower the sampling device to just below the well screen.
2. Remove the constriction from the device and allow the sample to fill the syringe, apply slight suction as necessary.
3. Bring unit to the surface. If necessary, transfer the sample to vials, as outlined in steps 2 through 7 above.

7.5 Filtering

For samples requiring filtering, such as total metals analysis, the filter must be decontaminated prior to and between uses. Filters work by two methods. A barrel filter such as the "Geotech" filter works with a bicycle pump, used to build up positive pressure in the chamber containing the sample which is then forced through the filter paper (minimum size 0.45 μm) into a jar placed underneath. The barrel itself is filled manually from the bailer or directly via the hose of the sampling pump. The pressure must be maintained up to 30 lbs/in² by periodic pumping.

A vacuum type filter involves two chambers; the upper chamber contains the sample and a filter (minimum size 0.45 μm) divides the chambers. Using a hand pump or a Gilian type pump, air is withdrawn from the lower chamber, creating a vacuum and thus causing the sample to move through the filter into the lower chamber where it is drained into a sample jar. Repeated pumping may be required to drain all the sample into the lower chamber. If preservation of the sample is necessary, this should be done after filtering.

7.6 Post Operation

After all samples are collected and preserved, the sampling equipment should be decontaminated prior to sampling another well to prevent cross-contamination of equipment and monitor wells between locations.

1. Decontaminate all equipment.
2. Replace sampling equipment in storage containers.
3. Prepare and transport ground water samples to the laboratory. Check sample documentation and make sure samples are properly packed for shipment.

7.7 Special Considerations for VOA Sampling

The proper collection of a sample for volatile organics requires minimal disturbance of the sample to limit volatilization and therefore a loss of volatiles from the sample.

Sample retrieval systems suitable for the valid collection of volatile organic samples are: positive displacement bladder pumps, gear driven submersible pumps, syringe samplers and bailers (Barcelona, 1984; Nielsen, 1985). Field conditions and other constraints will limit the choice of appropriate systems. The focus of concern must be to provide a valid sample for analysis, one which has been subjected to the least amount of turbulence possible.

The following procedures should be followed:

1. Open the vial, set cap in a clean place, and collect the sample during the middle of the cycle. When collecting duplicates, collect both samples at the same time.
2. Fill the vial to just overflowing. Do not rinse the vial, nor excessively overflow it. There should be a convex meniscus on the top of the vial.
3. Check that the cap has not been contaminated (splashed) and carefully cap the vial. Place the cap directly over the top and screw down firmly. Do not overtighten and break the cap.
4. Invert the vial and tap gently. Observe vial for at least ten (10) seconds. If an air bubble appears, discard the sample and begin again. It is imperative that no entrapped air is in the sample vial.
5. Immediately place the vial in the protective foam sleeve and place into the cooler, oriented so that it is lying on its side, not straight up.
6. The holding time for VOAs is seven days. Samples should be shipped or delivered to the laboratory daily so as not to exceed the holding time. Ensure that the samples remain at 4EC, but do not allow them to freeze.

8.0 CALCULATIONS

If it is necessary to calculate the volume of the well, utilize the following equation:

$$\text{Well volume} = \pi r^2 h (cf) \quad [Equation 1]$$

where:

$$\begin{aligned} \pi &= \text{pi} \\ r &= \text{radius of monitoring well (feet)} \\ h &= \text{height of the water column (feet)} \\ &\quad [\text{This may be determined by subtracting the depth to water from the total depth of the well as measured from the same reference point.}] \\ cf &= \text{conversion factor (gal/ft}^3\text{) = 7.48 gal/ft}^3 \text{ [In this equation, 7.48 gal/ft}^3 \text{ is the necessary conversion factor.]} \end{aligned}$$

Monitor well diameters are typically 2", 3", 4", or 6". Knowing the diameter of the monitor well, there are a number of standard conversion factors which can be used to simplify the equation above.

The volume, in gallons per linear foot, for various standard monitor well diameters can be calculated as follows:

$$v(\text{gal/ft}) = \pi r^2 (cf) \quad [Equation 2]$$

where:

$$\begin{aligned} \pi &= \text{pi} \\ r &= \text{radius of monitoring well (feet)} \\ cf &= \text{conversion factor (7.48 gal/ft}^3\text{)} \end{aligned}$$

For a 2" diameter well, the volume per linear foot can be calculated as follows:

$$\begin{aligned} \text{vol/linear ft} &= \pi r^2 (cf) \quad [Equation 2] \\ &= 3.14 (1/12 \text{ ft})^2 7.48 \text{ gal/ft}^3 \\ &= 0.1632 \text{ gal/ft} \end{aligned}$$

Remember that if you have a 2" diameter well, you must convert this to the radius in feet to be able to use the equation.

The conversion factors for the common size monitor wells are as follows:

Well diameter	2"	3"	4"	6"
Volume (gal/ft.)	0.1632	0.3672	0.6528	1.4688

If you utilize the conversion factors above, Equation

1 should be modified as follows:

$$\text{Well volume} = (h)(cf) \quad [\text{Equation 3}]$$

where:

h = height of water column (feet)
 cf = the conversion factor calculated from Equation 2

The well volume is typically tripled to determine the volume to be purged.

9.0 QUALITY ASSURANCE/ QUALITY CONTROL

There are no specific quality assurance (QA) activities which apply to the implementation of these procedures. However, the following general QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.
2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation and they must be documented.
3. The collection of rinsate blanks is recommended to evaluate potential for cross contamination from the purging and/or sampling equipment.
4. Trip blanks are required if analytical parameters include VOAs.

10.0 DATA VALIDATION

This section is not applicable to this SOP.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA or REAC health and safety guidelines. More specifically, depending upon the site specific contaminants, various protective programs

must be implemented prior to sampling the first well. The site health and safety plan should be reviewed with specific emphasis placed on the protection program planned for the well sampling tasks. Standard safe operating practices should be followed such as minimizing contact with potential contaminants in both the vapor phase and liquid matrix through the use of respirators and disposable clothing.

When working around volatile organic contaminants:

1. Avoid breathing constituents venting from the well.
2. Pre-survey the well head-space with an FID/PID prior to sampling.
3. If monitoring results indicate organic constituents, sampling activities may be conducted in Level C protection. At a minimum, skin protection will be afforded by disposable protective clothing.

Physical hazards associated with well sampling:

1. Lifting injuries associated with pump and bailers retrieval; moving equipment.
2. Use of pocket knives for cutting discharge hose.
3. Heat/cold stress as a result of exposure to extreme temperatures and protective clothing.
4. Slip, trip, fall conditions as a result of pump discharge.
5. Restricted mobility due to the wearing of protective clothing.
6. Electrical shock associated with use of submersible pumps is possible. Use a GFCI or a copper grounding stake to avoid this problem.

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SUPERFUND TECHNICAL ASSESSMENT RESPONSE TEAM STANDARD OPERATING PROCEDURES

SOP 301 DECONTAMINATION PROCEDURES

1.0 PURPOSE

To provide guidance for the decontamination of equipment used to sample, and install sample, and install sample points (monitor wells, soil borings and test pits), and make field measurements. This operating practice is not intended to be site specific or equipment specific, but to provide guidance in place of non-existent state or federal guidelines.

2.0 DISCUSSION

2.1 Introduction

The objective of decontamination procedures is to provide clean equipment for the retrieval of representative environmental samples. Decontamination procedures differ depending on the nature of the equipment used. The three categories of decontamination procedures are discussed below:

- Intrusive equipment used to install sample points including drilling (tools, augers, rods, etc.) and excavation equipment (backhoes, excavators, etc.).
- Equipment used to measure the characteristics of the media to be sampled including water level, pH, specific conductivity, and temperature probes. This category also includes pumps to purge water.
- Equipment that has contact with the sample to be submitted for laboratory analysis including bailer, split-spoons, hand auger, stainless steel bowls and scoops.

Because items from the first two categories do not contact the sample media that is sent to a laboratory for analysis, the decontamination procedures are less stringent. Dedicated and disposable equipment will be used whenever feasible to limit decontamination and the possibility of cross-contamination. This includes rope, tubing, filterware and, in some cases, soil scoops and bailers.

3.0 PROCEDURES

3.1 Intrusive Equipment

Drilling tools, including augers, rods, drill bits, hand tools, etc. will be steam cleaned prior to use and after each location. Split spoons will also be steam cleaned if not used

for sample collection. Backhoe buckets and arms will also be steam cleaned prior to use and between each sample location.

3.2 Field Measurement Equipment

Water level probes will be cleaned using the following procedures:

- Wipe the probe with a paper towel.
- Alconox and potable water wash.
- Deionized water rinse.

Other measurement equipment should be rinsed with deionized water between readings.

Pumps used for well purging shall be decontaminated using the following procedures:

- Alconox and potable water scrub and pump through.
- Potable water rinse and pump through.

Rope and tubing used with the pump will be made of polyethylene and be dedicated (and disposable) to one sample location.

3.3 Sampling Equipment

Equipment used for sample collection include but are not limited to:

- Teflon bailers.
- Stainless steel scoops and bowls.
- Hand augers.
- Split spoons.

This equipment will be cleaned using the following procedures:

- Alconox and potable water scrub.
- Thorough potable water rinse.
- Deionized water rinse.
- Total air dry

Sampling instruments should be wrapped in aluminum foil after decontamination to keep clean before sampling.

4.0 DOCUMENTATION

Decontamination efforts should be documented in the field logbook. Decontamination fluids should be disposed of properly. Depending on site conditions, it may be appropriate to contain spent decontamination fluids. In that case, the appropriate vessel (i.e., drum) should be used depending on the ultimate disposition of the material.

5.0 INTERPRETATION

If there are questions on the interpretation or applicability of items in this operating practice, the Project Manager or Technical Manager should be consulted. In the absence of either of those, contact a Section Manager.

6.0 REFERENCES

New Jersey Department of Environmental Protection and energy Field Sampling Procedures Manual, May 1992.

"Standard Practice for Decontamination of Field Equipment Used at Non-radioactive Waste Sites", ASTM Designation D5088-90.

Method 1669

**Sampling Ambient Water for Trace Metals at EPA Water Quality
Criteria Levels**

July 1996

**U.S. Environmental Protection Agency
Office of Water
Engineering and Analysis Division (4303)
401 M Street S.W.
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Disclaimer

This sampling method has been reviewed and approved for publication by the Analytical Methods Staff within the Engineering and Analysis Division of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Further Information

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Introduction

This sampling method was designed to support water quality monitoring programs authorized under the Clean Water Act. Section 304(a) of the Clean Water Act requires EPA to publish water quality criteria that reflect the latest scientific knowledge concerning the physical fate (e.g., concentration and dispersal) of pollutants, the effects of pollutants on ecological and human health, and the effect of pollutants on biological community diversity, productivity, and stability.

Section 303 of the Clean Water Act requires states to set a water quality standard for each body of water within its boundaries. A state water quality standard consists of a designated use or uses of a waterbody or a segment of a waterbody, the water quality criteria that are necessary to protect the designated use or uses, and an antidegradation policy. These water quality standards serve two purposes: (1) they establish the water quality goals for a specific waterbody, and (2) they are the basis for establishing water quality-based treatment controls and strategies beyond the technology-based controls required by Sections 301(b) and 306 of the Clean Water Act.

In defining water quality standards, the state may use narrative criteria, numeric criteria, or both. However, the 1987 amendments to the Clean Water Act required states to adopt numeric criteria for toxic pollutants (designated in Section 307(a) of the Act) based on EPA Section 304(a) criteria or other scientific data, when the discharge or presence of those toxic pollutants could reasonably be expected to interfere with designated uses.

In some cases, these water quality criteria are as much as 280 times lower than those achievable using existing EPA methods and required to support technology-based permits. Therefore, this sampling method, and the analytical methods referenced in Table 1 of this document, were developed by EPA to specifically address state needs for measuring toxic metals at water quality criteria levels, when such measurements are necessary to protect designated uses in state water quality standards. The latest criteria published by EPA are those listed in the National Toxics Rule (57 *FR* 60848) and the Stay of Federal Water Quality Criteria for Metals (60 *FR* 22228). These rules include water quality criteria for 13 metals, and it is these criteria on which this sampling method and the referenced analytical methods are based.

In developing these methods, EPA found that one of the greatest difficulties in measuring pollutants at these levels was precluding sample contamination during collection, transport, and analysis. The degree of difficulty, however, is highly dependent on the metal and site-specific conditions. This method, therefore, is designed to provide the level of protection necessary to preclude contamination in nearly all situations. It is also designed to provide the procedures necessary to produce reliable results at the lowest possible water quality criteria published by EPA. In recognition of the variety of situations to which this method may be applied, and in recognition of continuing technological advances, the method is performance-based. Alternative procedures may be used, so long as those procedures are demonstrated to yield reliable results.

Requests for additional copies of this method should be directed to:

U.S. EPA NCEPI
11029 Kenwood Road
Cincinnati, OH 45242
513/489-8190

Note: This document is intended as guidance only. Use of the terms "must," "may," and "should" are included to mean that EPA believes that these procedures must, may, or should be followed in order to produce the desired results when using this guidance. In addition, the guidance is intended to be performance-based, in that the use of less stringent procedures may be used so long as neither samples nor blanks are contaminated when following those modified procedures. Because the only way to measure the performance of the modified procedures is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the referenced methods, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected.

Method 1669

Sampling Ambient Water for Determination of Metals at EPA Water Quality Criteria Levels

1.0 Scope and Application

- 1.1 This method is for the collection and filtration of ambient water samples for subsequent determination of total and dissolved metals at the levels listed in Table 1. It is designed to support the implementation of water quality monitoring and permitting programs administered under the Clean Water Act.
- 1.2 This method is applicable to the metals listed below and other metals, metals species, and elements amenable to determination at trace levels.

Analyte	Symbol	Chemical Abstract Services Registry Number (CASRN)
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Cadmium	(Cd)	7440-43-9
Chromium (III)	Cr ⁺³	16065-83-1
Chromium (VI)	Cr ⁺⁶	18540-29-9
Copper	(Cu)	7440-50-8
Lead	(Pb)	7439-92-1
Mercury	(Hg)	7439-97-6
Nickel	(Ni)	7440-02-0
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Thallium	(Tl)	7440-28-0
Zinc	(Zn)	7440-66-6

- 1.3 This method is accompanied by the 1600 series methods listed in Table 1. These methods include the sample handling, analysis, and quality control procedures necessary for reliable determination of trace metals in aqueous samples.
- 1.4 This method is not intended for determination of metals at concentrations normally found in treated and untreated discharges from industrial facilities. Existing regulations (40 *CFR* Parts 400-500) typically limit concentrations in industrial discharges to the mid to high part-per-billion (ppb) range, whereas ambient metals concentrations are normally in the low part-per-trillion (ppt) to low ppb range. This guidance is therefore directed at the collection of samples to be measured at or near the levels listed in Table 1. Actual concentration ranges to which this guidance is applicable will be dependent on the sample matrix, dilution levels, and other laboratory operating conditions.
- 1.5 The ease of contaminating ambient water samples with the metal(s) of interest and interfering substances cannot be overemphasized. This method includes sampling techniques that should maximize the ability of the sampling team to collect samples reliably and eliminate sample contamination. These techniques are given in Section 8.0 and are based on findings of researchers performing trace metals analyses (References 1-9).

- 1.6 Clean and Ultraclean—The terms "clean" and "ultraclean" have been used in other Agency guidance to describe the techniques needed to reduce or eliminate contamination in trace metals determinations. These terms are not used in this sampling method due to a lack of exact definitions. However, the information provided in this method is consistent with summary guidance on clean and ultraclean techniques (Reference 10).
- 1.7 This sampling method follows the EPA Environmental Methods Management Council's "Format for Method Documentation" (Reference 11).
- 1.8 Method 1669 is "performance-based"; i.e., an alternate sampling procedure or technique may be used, so long as neither samples nor blanks are contaminated when following the alternate procedures. Because the only way to measure the performance of the alternate procedures is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the methods referenced in Table 1, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected. Section 9.2 provides additional details on the tests and documentation required to support equivalent performance.
- 1.9 For dissolved metal determinations, samples must be filtered through a 0.45 µm capsule filter at the field site. The filtering procedures are described in this method. The filtered samples may be preserved in the field or transported to the laboratory for preservation. Procedures for field preservation are detailed in this sampling method; procedures for laboratory preservation are provided in the methods referenced in Table 1. Preservation requirements are summarized in Table 2.
- 1.10 The procedures in this method are for use only by personnel thoroughly trained in the collection of samples for determination of metals at ambient water quality control levels.

2.0 Summary of Method

- 2.1 Before samples are collected, all sampling equipment and sample containers are cleaned in a laboratory or cleaning facility using detergent, mineral acids, and reagent water as described in the methods referenced in Table 1. The laboratory or cleaning facility is responsible for generating an acceptable equipment blank to demonstrate that the sampling equipment and containers are free from trace metals contamination before they are shipped to the field sampling team. An acceptable blank is one that is free from contamination below the minimum level (ML) specified in the referenced analytical method (Section 9.3).
- 2.2 After cleaning, sample containers are filled with weak acid solution, individually double-bagged, and shipped to the sampling site. All sampling equipment is also bagged for storage or shipment.

NOTE: EPA has found that, in some cases, it may be possible to empty the weak acid solution from the bottle immediately prior to transport to the field site. In this case, the bottle should be refilled with reagent water (Section 7.1).

- 2.3 The laboratory or cleaning facility must prepare a large carboy or other appropriate clean container filled with reagent water (Section 7.1) for use with collection of field blanks during sampling activities. The reagent-water-filled container should be shipped to the field site and handled as all other sample containers and sampling equipment. At least one field blank should be processed per site, or one per every ten samples, whichever is more frequent (Section 9.4). If samples are to be collected for determination of trivalent chromium, the sampling team processes additional QC aliquots are processed as described in Section 9.6.

- 2.4 Upon arrival at the sampling site, one member of the two-person sampling team is designated as "dirty hands"; the second member is designated as "clean hands." All operations involving contact with the sample bottle and transfer of the sample from the sample collection device to the sample bottle are handled by the individual designated as "clean hands." "Dirty hands" is responsible for preparation of the sampler (except the sample container itself), operation of any machinery, and for all other activities that do not involve direct contact with the sample.
- 2.5 All sampling equipment and sample containers used for metals determinations at or near the levels listed in Table 1 must be nonmetallic and free from any material that may contain metals.
- 2.6 Sampling personnel are required to wear clean, nontalc gloves at all times when handling sampling equipment and sample containers.
- 2.7 In addition to processing field blanks at each site, a field duplicate must be collected at each sampling site, or one field duplicate per every 10 samples, whichever is more frequent (Section 9.5). Section 9.0 gives a complete description of quality control requirements.
- 2.8 Sampling
- 2.8.1 Whenever possible, samples are collected facing upstream and upwind to minimize introduction of contamination.
- 2.8.2 Samples may be collected while working from a boat or while on land.
- 2.8.3 Surface samples are collected using a grab sampling technique. The principle of the grab technique is to fill a sample bottle by rapid immersion in water and capping to minimize exposure to airborne particulate matter.
- 2.8.4 Subsurface samples are collected by suction of the sample into an immersed sample bottle or by pumping the sample to the surface.
- 2.9 Samples for dissolved metals are filtered through a 0.45 μm capsule filter at the field site. After filtering, the samples are double-bagged and iced immediately. Sample containers are shipped to the analytical laboratory. The sampling equipment is shipped to the laboratory or cleaning facility for recleaning.
- 2.10 Acid preservation of samples is performed in the field or in the laboratory. Field preservation is necessary for determinations of trivalent chromium. It has also been shown that field preservation can increase sample holding times for hexavalent chromium to 30 days; therefore it is recommended that preservation of samples for hexavalent chromium be performed in the field. For other metals, however, the sampling team may prefer to utilize laboratory preservation of samples to expedite field operations and to minimize the potential for sample contamination.
- 2.11 Sampling activities must be documented through paper or computerized sample tracking systems.

3.0 Definitions

- 3.1 Apparatus—Throughout this method, the sample containers, sampling devices, instrumentation, and all other materials and devices used in sample collection, sample processing, and sample analysis activities will be referred to collectively as the Apparatus.

3.2 Definitions of other terms are given in the Glossary (Section 15.0) at the end of this method.

4.0 Contamination and Interferences

4.1 Contamination Problems in Trace Metals Analysis

4.1.1 Preventing ambient water samples from becoming contaminated during the sampling and analytical process is the greatest challenge faced in trace metals determinations. In recent years, it has been shown that much of the historical trace metals data collected in ambient water are erroneously high because the concentrations reflect contamination from sampling and analysis rather than ambient levels (Reference 12). Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace metals.

4.1.2 There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination during sampling include metallic or metal-containing sampling equipment, containers, labware (e.g. talc gloves that contain high levels of zinc), reagents, and deionized water; improperly cleaned and stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust from automobile exhaust, cigarette smoke, nearby roads, bridges, wires, and poles. Even human contact can be a source of trace metals contamination. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples that are directly exposed to exhalation (Reference 3).

4.2 Contamination Control

4.2.1 Philosophy—The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is nonmetallic and free from any material that may contain metals of concern.

4.2.1.1 The integrity of the results produced cannot be compromised by contamination of samples. Requirements and suggestions for controlling sample contamination are given in this sampling method and in the analytical methods referenced in Table 1.

4.2.1.2 Substances in a sample or in the surrounding environment cannot be allowed to contaminate the Apparatus used to collect samples for trace metals measurements. Requirements and suggestions for protecting the Apparatus are given in this sampling method and in the methods referenced in Table 1.

4.2.1.3 While contamination control is essential, personnel health and safety remain the highest priority. Requirements and suggestions for personnel safety are given in Section 5 of this sampling method and in the methods referenced in Table 1.

4.2.2 Avoiding contamination—The best way to control contamination is to completely avoid exposure of the sample and Apparatus to contamination in the first place. Avoiding exposure means performing operations in an area known to be free from contamination. Two of the most important factors in avoiding/reducing sample contamination are (1) an awareness of potential sources of contamination and (2) strict attention to work being performed. Therefore, it is imperative that the procedures described in this method be carried out by well

trained, experienced personnel. Documentation of training should be kept on file and readily available for review.

4.2.2.1 Minimize exposure—The Apparatus that will contact samples or blanks should only be opened or exposed in a clean room, clean bench, glove box, or clean plastic bag, so that exposure to atmospheric inputs is minimized. When not being used, the Apparatus should be covered with clean plastic wrap, stored in the clean bench or in a plastic box or glove box, or bagged in clean, colorless zip-type bags. Minimizing the time between cleaning and use will also reduce contamination.

4.2.2.2 Wear gloves—Sampling personnel must wear clean, nontalc gloves (Section 6.7) during all operations involving handling of the Apparatus, samples, and blanks. Only clean gloves may touch the Apparatus. If another object or substance is touched, the glove(s) must be changed before again handling the Apparatus. If it is even suspected that gloves have become contaminated, work must be halted, the contaminated gloves removed, and a new pair of clean gloves put on. Wearing multiple layers of clean gloves will allow the old pair to be quickly stripped with minimal disruption to the work activity.

4.2.2.3 Use metal-free Apparatus—All Apparatus used for metals determinations at the levels listed in Table 1 must be nonmetallic and free of material that may contain metals. When it is not possible to obtain equipment that is completely free of the metal(s) of interest, the sample should not come into direct contact with the equipment.

4.2.2.3.1 Construction materials—Only the following materials should come in contact with samples: fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, polysulfone, polypropylene, or ultrapure quartz. PTFE is less desirable than FEP because the sintered material in PTFE may contain contaminants and is susceptible to serious memory effects (Reference 6). Fluoropolymer or glass containers should be used for samples that will be analyzed for mercury because mercury vapors can diffuse in or out of other materials, resulting either in contamination or low-biased results (Reference 3). Metal must not be used under any circumstance. Regardless of construction, all materials that will directly or indirectly contact the sample must be cleaned using the procedures described in the referenced analytical methods (see Table 1) and must be known to be clean and metal-free before proceeding.

4.2.2.3.2 The following materials have been found to contain trace metals and must not be used to hold liquids that come in contact with the sample or must not contact the sample, unless these materials have been shown to be free of the metals of interest at the desired level: Pyrex, Kimax, methacrylate, polyvinylchloride, nylon, and Vycor (Reference 6). In addition, highly colored plastics, paper cap liners, pigments used to mark increments on plastics, and rubber all contain trace levels of metals and must be avoided (Reference 13).

- 4.2.2.3.3 **Serialization**—Serial numbers should be indelibly marked or etched on each piece of Apparatus so that contamination can be traced, and logbooks should be maintained to track the sample from the container through the sampling process to shipment to the laboratory. Chain-of-custody procedures may also be used if warranted so that contamination can be traced to particular handling procedures or lab personnel.
- 4.2.2.3.4 The Apparatus should be clean when the sampling team receives it. If there are any indications that the Apparatus is not clean (e.g., a ripped storage bag), an assessment of the likelihood of contamination must be made. Sampling must not proceed if it is possible that the Apparatus is contaminated. If the Apparatus is contaminated, it must be returned to the laboratory or cleaning facility for proper cleaning before any sampling activity resumes.
- 4.2.2.3.5 Details for recleaning the Apparatus between collection of individual samples are provided in Section 10.0.
- 4.2.2.4 **Avoid sources of contamination**—Avoid contamination by being aware of potential sources and routes of contamination.
 - 4.2.2.4.1 **Contamination by carryover**—Contamination may occur when a sample containing low concentrations of metals is processed immediately after a sample containing relatively high concentrations of these metals. At sites where more than one sample will be collected, the sample known or expected to contain the lowest concentration of metals should be collected first with the sample containing the highest levels collected last (Section 8.1.4). This will help minimize carryover of metals from high- concentration samples to low- concentration samples. If the sampling team does not have prior knowledge of the waterbody, or when necessary, the sample collection system should be rinsed with dilute acid and reagent water between samples and followed by collection of a field blank (Section 10.3).
 - 4.2.2.4.2 **Contamination by samples**—Significant contamination of the Apparatus may result when untreated effluents, in-process waters, landfill leachates, and other samples containing mid- to high-level concentrations of inorganic substances are processed. As stated in Section 1.0, this sampling method is not intended for application to these samples, and samples containing high concentrations of metals must not be collected, processed, or shipped at the same time as samples being collected for trace metals determinations.
 - 4.2.2.4.3 **Contamination by indirect contact**—Apparatus that may not directly contact samples may still be a source of contamination. For example, clean tubing placed in a dirty plastic bag may pick up contamination from the bag and subsequently transfer the contamination to the sample. Therefore, it is imperative that every

piece of the Apparatus that is directly or indirectly used in the collection of ambient water samples be cleaned as specified in the analytical method(s) referenced in Table 1.

- 4.2.2.4.4 Contamination by airborne particulate matter—Less obvious substances capable of contaminating samples include airborne particles. Samples may be contaminated by airborne dust, dirt, particulate matter, or vapors from automobile exhaust; cigarette smoke; nearby corroded or rusted bridges, pipes, poles, or wires; nearby roads; and even human breath (Section 4.1.2). Whenever possible, the sampling activity should occur as far as possible from sources of airborne contamination (Section 8.1.3). Areas where nearby soil is bare and subject to wind erosion should be avoided.

- 4.3 Interferences—Interferences resulting from samples will vary considerably from source to source, depending on the diversity of the site being sampled. If a sample is suspected of containing substances that may interfere in the determination of trace metals, sufficient sample should be collected to allow the laboratory to identify and overcome interference problems.

5.0 Safety

- 5.1 The toxicity or carcinogenicity of the chemicals used in this method has not been precisely determined; however, these chemicals should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. Sampling teams are responsible for maintaining a current awareness file of OSHA regulations for the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets should also be made available to all personnel involved in sampling. It is also suggested that the organization responsible perform personal hygiene monitoring of each sampling team member who uses this method and that the results of this monitoring be made available to the member.
- 5.2 Operating in and around waterbodies carries the inherent risk of drowning. Life jackets must be worn when operating from a boat, when sampling in more than a few feet of water, or when sampling in swift currents.
- 5.3 Collecting samples in cold weather, especially around cold water bodies, carries the risk of hypothermia, and collecting samples in extremely hot and humid weather carries the risk of dehydration and heat stroke. Sampling team members should wear adequate clothing for protection in cold weather and should carry an adequate supply of water or other liquids for protection against dehydration in hot weather.

6.0 Apparatus and Materials

NOTE: Brand names, suppliers, and part numbers are for illustration only and no endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here. Meeting the performance requirements of this method is the responsibility of the sampling team and laboratory.

- 6.1 All sampling equipment and sample containers must be precleaned in a laboratory or cleaning facility, as described in the methods referenced in Table 1, before they are shipped to the field site.

Performance criteria for equipment cleaning is described in the referenced methods. To minimize difficulties in sampling, the equipment should be packaged and arranged to minimize field preparation.

- 6.2 Materials such as gloves (Section 6.7), storage bags (Section 6.8), and plastic wrap (Section 6.9), may be used new without additional cleaning unless the results of the equipment blank pinpoint any of these materials as a source of contamination. In this case, either a different supplier must be obtained or the materials must be cleaned.

- 6.3 Sample Bottles—Fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, or polypropylene; 500 mL or 1 L with lids. If mercury is a target analyte, fluoropolymer or glass bottles should be used. Refer to the methods referenced in Table 1 for bottle cleaning procedures.

6.3.1 Cleaned sample bottles should be filled with 0.1% HCl (v/v). In some cases, it may be possible to empty the weak acid solution from the sample bottle immediately prior to transport to the field site. In this case, the bottle should be refilled with reagent water (Section 7.1).

6.3.2 Whenever possible, sampling devices should be cleaned and prepared for field use in a class 100 clean room. Preparation of the devices in the field should be done within the glove bag (Section 6.6). Regardless of design, sampling devices must be constructed of nonmetallic material (Section 4.2.2.3.1) and free from material that contains metals. Fluoropolymer or other material shown not to adsorb or contribute mercury must be used if mercury is a target analyte; otherwise, polyethylene, polycarbonate, or polypropylene are acceptable. Commercially available sampling devices may be used provided that any metallic or metal-containing parts are replaced with parts constructed of nonmetallic material.

- 6.4 Surface Sampling Devices—Surface samples are collected using a grab sampling technique. Samples may be collected manually by direct submersion of the bottle into the water or by using a grab sampling device. Examples of grab samplers are shown in Figures 1 and 2 and may be used at sites where depth profiling is neither practical nor necessary.

6.4.1 The grab sampler in Figure 1 consists of a heavy fluoropolymer collar fastened to the end of a 2-m-long polyethylene pole, which serves to remove the sampling personnel from the immediate vicinity of the sampling point. The collar holds the sample bottle. A fluoropolymer closing mechanism, threaded onto the bottle, enables the sampler to open and close the bottle under water, thereby avoiding surface microlayer contamination (Reference 14). Polyethylene, polycarbonate, and polypropylene are also acceptable construction materials unless mercury is a target analyte. Assembly of the cleaned sampling device is as follows (refer to Figure 1):

6.4.1.1 Thread the pull cord (with the closing mechanism attached) through the guides and secure the pull ring with a simple knot. Screw a sample bottle onto the closing device and insert the bottle into the collar. Cock the closing plate so that the plate is pushed away from the operator.

6.4.1.2 The cleaned and assembled sampling device should be stored in a double layer of large, clean zip-type polyethylene bags or wrapped in two layers of clean polyethylene wrap if it will not be used immediately.

- 6.4.2 An alternate grab sampler design is shown in Figure 2. This grab sampler is used for discrete water samples and is constructed so that a capped clean bottle can be submerged, the cap

removed, sample collected, and bottle recapped at a selected depth. This device eliminates sample contact with conventional samplers (e.g., Niskin bottles), thereby reducing the risk of extraneous contamination. Because a fresh bottle is used for each sample, carryover from previous samples is eliminated (Reference 15).

6.5 Subsurface Sampling Devices—Subsurface sample collection may be appropriate in lakes and sluggish deep river environments or where depth profiling is determined to be necessary. Subsurface samples are collected by pumping the sample into a sample bottle. Examples of subsurface collection systems include the jar system device shown in Figure 3 and described in Section 6.5.1 or the continuous-flow apparatus shown in Figure 4 and described in Section 6.5.2.

6.5.1 Jar sampler (Reference 14)—The jar sampler (Figure 3) is comprised of a heavy fluoropolymer 1-L jar with a fluoropolymer lid equipped with two 1/4 in. fluoropolymer fittings. Sample enters the jar through a short length of fluoropolymer tubing inserted into one fitting. Sample is pulled into the jar by pumping on fluoropolymer tubing attached to the other fitting. A thick fluoropolymer plate supports the jar and provides attachment points for a fluoropolymer safety line and fluoropolymer torpedo counterweight.

6.5.1.1 Advantages of the jar sampler for depth sampling are (1) all wetted surfaces are fluoropolymer and can be rigorously cleaned; (2) the sample is collected into a sample jar from which the sample is readily recovered, and the jar can be easily recleaned; (3) the suction device (a peristaltic or rotary vacuum pump, Section 6.15) is located in the boat, isolated from the sampling jar; (4) the sampling jar can be continuously flushed with sample, at sampling depth, to equilibrate the system; and (5) the sample does not travel through long lengths of tubing that are more difficult to clean and keep clean (Reference 14). In addition, the device is designed to eliminate atmospheric contact with the sample during collection.

6.5.1.2 To assemble the cleaned jar sampler, screw the torpedo weight onto the machined bolt attached to the support plate of the jar sampler. Attach a section of the 1/4 in. o.d. tubing to the jar by inserting the tubing into the fitting on the lid and pushing down into the jar until approximately 8 cm from the bottom. Tighten the fitting nut securely. Attach the solid safety line to the jar sampler using a bowline knot to the loop affixed to the support plate.

6.5.1.3 For the tubing connecting the pump to the sampler, tubing lengths of up to 12 m have been used successfully (Reference 14).

6.5.2 Continuous-flow sampler (References 16-17)—This sampling system, shown in Figure 4, consists of a peristaltic or submersible pump and one or more lengths of precleaned fluoropolymer or styrene/ethylene/butylene/ silicone (SEBS) tubing. A filter is added to the sampling train when sampling for dissolved metals.

6.5.2.1 Advantages of this sampling system include (1) all wetted surfaces are fluoropolymer or SEBS and can be readily cleaned; (2) the suction device is located in the boat, isolated from the sample bottle; (3) the sample does not travel through long lengths of tubing that are difficult to clean and keep clean; and (4) in-line filtration is possible, minimizing field handling requirements for dissolved metals samples.

6.5.2.2 The sampling team assembles the system in the field as described in Section 8.2.8. System components include an optional polyethylene pole to remove sampling personnel from the immediate vicinity of the sampling point and the pump, tubing, filter, and filter holder listed in Sections 6.14 and 6.15.

- 6.6 Field-Portable Glove Bag—I2R, Model R-37-37H (nontalc), or equivalent. Alternately, a portable glove box may be constructed with a nonmetallic (PVC pipe or other suitable material) frame and a frame cover made of an inexpensive, disposable, nonmetallic material (e.g., a thin-walled polyethylene bag) (Reference 7).
- 6.7 Gloves—Clean, nontalc polyethylene, latex, vinyl, or PVC; various lengths. Shoulder-length gloves are needed if samples are to be collected by direct submersion of the sample bottle into the water or when sampling for mercury.
 - 6.7.1 Gloves, shoulder-length polyethylene—Associated Bag Co., Milwaukee, WI, 66-3-301, or equivalent.
 - 6.7.2 Gloves, PVC—Fisher Scientific Part No. 11-394-100B, or equivalent.
- 6.8 Storage Bags—Clean, zip-type, nonvented, colorless polyethylene (various sizes).
- 6.9 Plastic Wrap—Clean, colorless polyethylene.
- 6.10 Cooler—Clean, nonmetallic, with white interior for shipping samples.
- 6.11 Ice or Chemical Refrigerant Packs—To keep samples chilled in the cooler during shipment.
- 6.12 Wind Suit—Pamida, or equivalent.

NOTE: *This equipment is necessary only for collection of metals, such as mercury, that are known to have elevated atmospheric concentrations.*

- 6.12.1 An unlined, long-sleeved wind suit consisting of pants and jacket and constructed of nylon or other synthetic fiber is worn when sampling for mercury to prevent mercury adsorbed onto cotton or other clothing materials from contaminating samples.
 - 6.12.2 Washing and drying—The wind suit is washed by itself or with other wind suits only in a home or commercial washing machine and dried in a clothes dryer. The clothes dryer must be thoroughly vacuumed, including the lint filter, to remove all traces of lint before drying. After drying, the wind suit is folded and stored in a clean polyethylene bag for shipment to the sample site.
- 6.13 Boat
 - 6.13.1 For most situations (e.g., most metals under most conditions), the use of an existing, available boat is acceptable. A flat-bottom, Boston Whaler-type boat is preferred because sampling materials can be stored with reduced chance of tipping.

- 6.13.1.1 Immediately before use, the boat should be washed with water from the sampling site away from any sampling points to remove any dust or dirt accumulation.
- 6.13.1.2 Samples should be collected upstream of boat movement.
- 6.13.2 For mercury, and for situations in which the presence of contaminants cannot otherwise be controlled below detectable levels, the following equipment and precautions may be necessary:
 - 6.13.2.1 A metal-free (e.g., fiberglass) boat, along with wooden or fiberglass oars. Gasoline- or diesel-fueled boat motors should be avoided when possible because the exhaust can be a source of contamination. If the body of water is large enough to require use of a boat motor, the engine should be shut off at a distance far enough from the sampling point to avoid contamination, and the sampling team should manually propel the boat to the sampling point. Samples should be collected upstream of boat movement.
 - 6.13.2.2 Before first use, the boat should be cleaned and stored in an area that minimizes exposure to dust and atmospheric particles. For example, cleaned boats should not be stored in an area that would allow exposure to automobile exhaust or industrial pollution.
 - 6.13.2.3 The boat should be frequently visually inspected for possible contamination.
 - 6.13.2.4 After sampling, the boat should be returned to the laboratory or cleaning facility, cleaned as necessary, and stored away from any sources of contamination until next use.
- 6.14 Filtration Apparatus—Required when collecting samples for dissolved metals determinations.
 - 6.14.1 Filter—0.45 μm , 15 mm diameter or larger, tortuous-path capsule filters (Reference 18), Gelman Supor 12175, or equivalent.
 - 6.14.2 Filter holder—For mounting filter to the gunwale of the boat. Rod or pipe made from plastic material and mounted with plastic clamps.

NOTE: A filter holder may not be required if one or a few samples are to be collected. For these cases, it may only be necessary to attach the filter to the outlet of the tubing connected to the pump.

- 6.15 Pump and Pump Apparatus—Required for use with the jar sampling system (Section 6.5.1) or the continuous-flow system (Section 6.5.2). Peristaltic pump; 115 V a.c., 12 V d.c., internal battery, variable-speed, single-head, Cole-Parmer, portable, "Masterflex L/S," Catalog No. H-07570-10 drive with Quick Load pump head, Catalog No. H-07021-24, or equivalent.

NOTE: Equivalent pumps may include rotary vacuum, submersible, or other pumps free from metals and suitable to meet the site-specific depth sampling needs.

- 6.15.1 Cleaning—Peristaltic pump modules do not require cleaning. However, nearly all peristaltic pumps contain a metal head and metal controls. Touching the head or controls necessitates

changing of gloves before touching the Apparatus. If a submersible pump is used, a large volume of sample should be pumped to clean the stainless steel shaft (hidden behind the impeller) that comes in contact with the sample. Pumps with metal impellers should not be used.

- 6.15.2 Tubing—For use with peristaltic pump. SEBS resin, approximately 3/8 in. i.d. by approximately 3 ft, Cole-Parmer size 18, Cat. No. G-06464-18, or approximately 1/4 in. i.d., Cole-Parmer size 17, Catalog No. G-06464-17, or equivalent. Tubing is cleaned by soaking in 5-10% HCl solution for 8-24 hours, rinsing with reagent water in a clean bench in a clean room, and drying in the clean bench by purging with mercury-free air or nitrogen. After drying, the tubing is double-bagged in clear polyethylene bags, serialized with a unique number, and stored until use.
- 6.15.3 Tubing—For connection to peristaltic pump tubing. Fluoropolymer, 3/8 or 1/4 in. o.d., in lengths as required to reach the point of sampling. If sampling will be at some depth from the end of a boom extended from a boat, sufficient tubing to extend to the end of the boom and to the depth will be required. Cleaning of the fluoropolymer can be the same as cleaning the tubing for the rotary vacuum pump (Section 6.15.1.2). If necessary, more aggressive cleaning (e.g., concentrated nitric acid) may be used.
- 6.15.4 Batteries to operate submersible pump—12 V, 2.6 amp, gel cell, YUASA NP2.6-12, or equivalent. A 2 amp fuse connected at the positive battery terminal is strongly recommended to prevent short circuits from overheating the battery. A 12 V, lead-acid automobile or marine battery may be more suitable for extensive pumping.
- 6.15.5 Tubing connectors—Appropriately sized PVC, clear polyethylene, or fluoropolymer "barbed" straight connectors cleaned as the tubing above. Used to connect multiple lengths of tubing.
- 6.16 Carboy—For collection and storage of dilute waste acids used to store bottles.
- 6.17 Apparatus—For field preservation of aliquots for trivalent chromium determinations.
 - 6.17.1 Fluoropolymer forceps—1 L fluoropolymer jar, and 30 mL fluoropolymer vials with screw-caps (one vial per sample and blank). It is recommended that 1 mL of ultrapure nitric acid (Section 7.3) be added to each vial prior to transport to the field to simplify field handling activities (See Section 8.4.4.6).
 - 6.17.2 Filters—0.4 μ m, 47 mm polycarbonate Nuclepore (or equivalent). Filters are cleaned as follows. Fill a 1 L fluoropolymer jar approximately two-thirds full with 1 N nitric acid. Using fluoropolymer forceps, place individual filters in the fluoropolymer jar. Allow the filters to soak for 48 hours. Discard the acid, and rinse five times with reagent water. Fill the jar with reagent water, and soak the filters for 24 hours. Remove the filters when ready for use, and using fluoropolymer forceps, place them on the filter apparatus (Section 6.17.3).
 - 6.17.3 Vacuum filtration apparatus—Millipore 47 mm size, or equivalent, vacuum pump and power source (and extension cords, if necessary) to operate the pump.
 - 6.17.4 Eppendorf auto pipet and colorless pipet tips (100-1000 μ L)
 - 6.17.5 Wrist-action shaker—Burrel or equivalent.

6.17.6 Fluoropolymer wash bottles—One filled with reagent water (Section 7.1) and one filled with high-purity 10% HCl (Section 7.4.4), for use in rinsing forceps and pipet tips.

7.0 Reagents and Standards

- 7.1 Reagent Water—Water in which the analytes of interest and potentially interfering substances are not detected at the Method Detection Limit (MDL) of the analytical method used for analysis of samples. Prepared by distillation, deionization, reverse osmosis, anodic/cathodic stripping voltammetry, or other techniques that remove the metal(s) and potential interferent(s). A large carboy or other appropriate container filled with reagent water must be available for the collection of field blanks.
- 7.2 Nitric Acid—Dilute, trace-metal grade, shipped with sampling kit for cleaning equipment between samples.
- 7.3 Sodium Hydroxide—Concentrated, 50% solution for use when field-preserving samples for hexavalent chromium determinations (Section 8.4.5).
- 7.4 Reagents—For field-processing aliquots for trivalent chromium determinations
- 7.4.1 Nitric Acid, Ultrapure—For use when field-preserving samples for trivalent chromium determinations (Sections 6.17 and 8.4.4).
- 7.4.2 Ammonium Iron (II) Sulfate Solution (0.01M)—Used to prepare the chromium (III) extraction solution (Section 7.4.3) necessary for field preservation of samples for trivalent chromium (Section 8.4.4). Prepare the ammonium iron (II) sulfate solution by adding 3.92 g ammonium iron (II) sulfate (ultrapure grade) to a 1 L volumetric flask. Bring to volume with reagent water. Store in a clean polyethylene bottle.
- 7.4.3 Chromium (III) extraction solution—For use when field-preserving samples for trivalent chromium determinations (Section 8.4.4). Prepare this solution by adding 100 mL of ammonium iron (II) sulfate solution (Section 7.4.2) to a 125 mL polyethylene bottle. Adjust pH to 8 with approximately 2 mL of ammonium hydroxide solution. Cap and shake on a wrist-action shaker for 24 hours. This iron (III) hydroxide solution is stable for 30 days.
- 7.4.4 Hydrochloric acid—High-purity, 10% solution, shipped with sampling kit in fluoropolymer wash bottles for cleaning trivalent chromium sample preservation equipment between samples.
- 7.4.5 Chromium stock standard solution (1000 µg/mL)—Prepared by adding 3.1 g anhydrous chromium chloride to a 1 L flask and diluting to volume with 1% hydrochloric acid. Store in polyethylene bottle. A commercially available standard solution may be substituted.
- 7.4.6 Standard chromium spike solution (1000 µg/L)—Used to spike sample aliquots for matrix spike/matrix spike duplicate (MS/MSD) analysis and to prepare ongoing precision and recovery standards. Prepared by spiking 1 mL of the chromium stock standard solution (Section 7.4.5) into a 1 L flask. Dilute to volume with 1% HCl. Store in a polyethylene bottle.
- 7.4.7 Ongoing precision and recovery (OPR) standard (25 µg/L)—Prepared by spiking 2.5 mL of the standard chromium spike solution (Section 7.4.6) into a 100 mL flask. Dilute to volume with 1% HCl. One OPR is required for every 10 samples.

8.0 Sample Collection, Filtration, and Handling

8.1 Site Selection

8.1.1 Selection of a representative site for surface water sampling is based on many factors including: study objectives, water use, point source discharges, non-point source discharges, tributaries, changes in stream characteristics, types of stream bed, stream depth, turbulence, and the presence of structures (bridges, dams, etc.). When collecting samples to determine ambient levels of trace metals, the presence of potential sources of metal contamination are of extreme importance in site selection.

8.1.2 Ideally, the selected sampling site will exhibit a high degree of cross-sectional homogeneity. It may be possible to use previously collected data to identify locations for samples that are well mixed or are vertically or horizontally stratified. Since mixing is principally governed by turbulence and water velocity, the selection of a site immediately downstream of a riffle area will ensure good vertical mixing. Horizontal mixing occurs in constrictions in the channel. In the absence of turbulent areas, the selection of a site that is clear of immediate point sources, such as industrial effluents, is preferred for the collection of ambient water samples (Reference 19).

8.1.3 To minimize contamination from trace metals in the atmosphere, ambient water samples should be collected from sites that are as far as possible (e.g., at least several hundred feet) from any metal supports, bridges, wires or poles. Similarly, samples should be collected as far as possible from regularly or heavily traveled roads. If it is not possible to avoid collection near roadways, it is advisable to study traffic patterns and plan sampling events during lowest traffic flow (Reference 7).

8.1.4 The sampling activity should be planned to collect samples known or suspected to contain the lowest concentrations of trace metals first, finishing with the samples known or suspected to contain the highest concentrations. For example, if samples are collected from a flowing river or stream near an industrial or municipal discharge, the upstream sample should be collected first, the downstream sample collected second, and the sample nearest the discharge collected last. If the concentrations of pollutants is not known and cannot be estimated, it is necessary to use precleaned sampling equipment at each sampling location.

8.2 Sample Collection Procedure—Before collecting ambient water samples, consideration should be given to the type of sample to be collected, the amount of sample needed, and the devices to be used (grab, surface, or subsurface samplers). Sufficient sample volume should be collected to allow for necessary quality control analyses, such as matrix spike/matrix spike duplicate analyses.

8.2.1 Four sampling procedures are described:

8.2.1.1 Section 8.2.5 describes a procedure for collecting samples directly into the sample container. This procedure is the simplest and provides the least potential for contamination because it requires the least amount of equipment and handling.

8.2.1.2 Section 8.2.6 describes a procedure for using a grab sampling device to collect samples.

8.2.1.3 Section 8.2.7 describes a procedure for depth sampling with a jar sampler. The size of sample container used is dependent on the amount of sample needed by the analytical laboratory.

8.2.1.4 Section 8.2.8 describes a procedure for continuous-flow sampling using a submersible or peristaltic pump.

8.2.2 The sampling team should ideally approach the site from down current and downwind to prevent contamination of the sample by particles sloughing off the boat or equipment. If it is not possible to approach from both, the site should be approached from down current if sampling from a boat or approached from downwind if sampling on foot. When sampling from a boat, the bow of the boat should be oriented into the current (the boat will be pointed upstream). All sampling activity should occur from the bow.

If the samples are being collected from a boat, it is recommended that the sampling team create a stable workstation by arranging the cooler or shipping container as a work table on the upwind side of the boat, covering this worktable and the upwind gunnel with plastic wrap or a plastic tablecloth, and draping the wrap or cloth over the gunnel. If necessary, duct tape is used to hold the wrap or cloth in place.

8.2.3 All operations involving contact with the sample bottle and with transfer of the sample from the sample collection device to the sample bottle (if the sample is not directly collected in the bottle) are handled by the individual designated as "clean hands." "Dirty hands" is responsible for all activities that do not involve direct contact with the sample.

Although the duties of "clean hands" and "dirty hands" would appear to be a logical separation of responsibilities, in fact, the completion of the entire protocol may require a good deal of coordination and practice. For example, "dirty hands" must open the box or cooler containing the sample bottle and unzip the outer bag; clean hands must reach into the outer bag, open the inner bag, remove the bottle, collect the sample, replace the bottle lid, put the bottle back into the inner bag, and zip the inner bag. "Dirty hands" must close the outer bag and place it in a cooler.

To minimize unnecessary confusion, it is recommended that a third team member be available to complete the necessary sample documentation (e.g., to document sampling location, time, sample number, etc). Otherwise, "dirty hands" must perform the sample documentation activity (Reference 7).

8.2.4 Extreme care must be taken during all sampling operations to minimize exposure of the sample to human, atmospheric, and other sources of contamination. Care must be taken to avoid breathing directly on the sample, and whenever possible, the sample bottle should be opened, filled, and closed while submerged.

8.2.5 Manual collection of surface samples directly into the sample bottle.

8.2.5.1 At the site, all sampling personnel must put on clean gloves (Section 6.7) before commencing sample collection activity, with "clean hands" donning shoulder-length gloves. If samples are to be analyzed for mercury, the sampling team must also put their precleaned wind suits on at this time. Note that "clean hands" should put on the

shoulder-length polyethylene gloves (Section 6.7.1) and both "clean hands" and "dirty hands" should put on the PVC gloves (Section 6.7.2).

8.2.5.2 "Dirty hands" must open the cooler or storage container, remove the double-bagged sample bottle from storage, and unzip the outer bag.

8.2.5.3 Next, "clean hands" opens the inside bag containing the sample bottle, removes the bottle, and reseals the inside bag. "Dirty hands" then reseals the outer bag.

8.2.5.4 "Clean hands" unscrews the cap and, while holding the cap upside down, discards the dilute acid solution from the bottle into a carboy for wastes (Section 6.16) or discards the reagent water directly into the water body.

8.2.5.5 "Clean hands" then submerges the sample bottle, and allows the bottle to partially fill with sample. "Clean hands" screws the cap on the bottle, shakes the bottle several times, and empties the rinsate away from the site. After two more rinsings, "clean hands" holds the bottle under water and allows bottle to fill with sample. After the bottle has filled (i.e., when no more bubbles appear), and while the bottle is still inverted so that the mouth of the bottle is underwater, "clean hands" replaces the cap of the bottle. In this way, the sample has never contacted the air.

8.2.5.6 Once the bottle lid has been replaced, "dirty hands" reopens the outer plastic bag, and "clean hands" opens the inside bag, places the bottle inside it, and zips the inner bag.

8.2.5.7 "Dirty hands" zips the outer bag.

8.2.5.8 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

8.2.5.9 If the sample is to be analyzed for dissolved metals, it is filtered in accordance with the procedure described in Section 8.3.

8.2.6 Sample collection with grab sampling device—The following steps detail sample collection using the grab sampling device shown in Figure 1 and described in Section 6.4.1. The procedure is indicative of the "clean hands/dirty hands" technique that must be used with alternative grab sampling devices such as that shown in Figure 2 and described in Section 6.4.2.

8.2.6.1 The sampling team puts on gloves (and wind suits, if applicable). Ideally, a sample bottle will have been preattached to the sampling device in the class 100 clean room at the laboratory. If it is necessary to attach a bottle to the device in the field, "clean hands" performs this operation, described in Section 6.4.2, inside the field-portable glove bag (Section 6.6).

8.2.6.2 "Dirty hands" removes the sampling device from its storage container and opens the outer polyethylene bag.

8.2.6.3 "Clean hands" opens the inside polyethylene bag and removes the sampling device.

- 8.2.6.4 "Clean hands" changes gloves.
 - 8.2.6.5 "Dirty hands" submerges the sampling device to the desired depth and pulls the fluoropolymer pull cord to bring the seal plate into the middle position so that water can enter the bottle.
 - 8.2.6.6 When the bottle is full (i.e., when no more bubbles appear), "dirty hands" pulls the fluoropolymer cord to the final stop position to seal off the sample and removes the sampling device from the water.
 - 8.2.6.7 "Dirty hands" returns the sampling device to its large inner plastic bag, "clean hands" pulls the bottle out of the collar, unscrews the bottle from the sealing device, and caps the bottle. "Clean hands" and "dirty hands" then return the bottle to its double-bagged storage as described in Sections 8.2.5.6 through 8.2.5.7.
 - 8.2.6.8 Closing mechanism—"Clean hands" removes the closing mechanism from the body of the grab sampler, rinses the device with reagent water (Section 7.1), places it inside a new clean plastic bag, zips the bag, and places the bag inside an outer bag held by "dirty hands." "Dirty hands" zips the outer bag and places the double-bagged closing mechanism in the equipment storage box.
 - 8.2.6.9 Sampling device—"Clean hands" seals the large inside bag containing the collar, pole, and cord and places the bag into a large outer bag held by "dirty hands." "Dirty hands" seals the outside bag and places the double-bagged sampling device into the equipment storage box.
 - 8.2.6.10 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.
 - 8.2.6.11 If the sample is to be analyzed for dissolved metals, it is filtered in accordance with the procedures described in Section 8.3.
- 8.2.7 Depth sampling using a jar sampling device (Figure 3 and Section 6.5.1)
- 8.2.7.1 The sampling team puts on gloves (and wind suits, if applicable) and handles bottles as with manual collection (Sections 8.2.5.1 through 8.2.5.4 and 8.2.5.6 through 8.2.5.7).
 - 8.2.7.2 "Dirty hands" removes the jar sampling device from its storage container and opens the outer polyethylene bag.
 - 8.2.7.3 "Clean hands" opens the inside polyethylene bag and removes the jar sampling apparatus. Ideally, the sampling device will have been preassembled in a class 100 clean room at the laboratory. If, however, it is necessary to assemble the device in the field, "clean hands" must perform this operation, described in Section 6.5.2, inside a field-portable glove bag (Section 6.6).
 - 8.2.7.4 While "dirty hands" is holding the jar sampling apparatus, "clean hands" connects the pump to the to the 1/4 in. o.d. flush line.

- 8.2.7.5 "Dirty hands" lowers the weighted sampler to the desired depth.
- 8.2.7.6 "Dirty hands" turns on the pump allowing a large volume (>2 L) of water to pass through the system.
- 8.2.7.7 After stopping the pump, "dirty hands" pulls up the line, tubing, and device and places them into either a field-portable glove bag or a large, clean plastic bag as they emerge.
- 8.2.7.8 Both "clean hands" and "dirty hands" change gloves.
- 8.2.7.9 Using the technique described in Sections 8.2.5.2 through 8.2.5.4, the sampling team removes a sample bottle from storage, and "clean hands" places the bottle into the glove bag.
- 8.2.7.10 "Clean hands" tips the sampling jar and dispenses the sample through the short length of fluoropolymer tubing into the sample bottle.
- 8.2.7.11 Once the bottle is filled, "clean hands" replaces the cap of the bottle, returns the bottle to the inside polyethylene bag, and zips the bag. "Clean hands" returns the zipped bag to the outside polyethylene bag held by "dirty hands."
- 8.2.7.12 "Dirty hands" zips the outside bag. If the sample is to be analyzed for dissolved metals, it is filtered as described in Section 8.3.
- 8.2.7.13 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.
- 8.2.8 Continuous-flow sampling (Figure 4 and Section 6.5.2)—The continuous-flow sampling system uses peristaltic pump (Section 6.15) to pump sample to the boat or to shore through the SEBS-resin or PTFE tubing.
 - 8.2.8.1 Before putting on wind suits or gloves, the sampling team removes the bags containing the pump (Section 6.15), SEBS-resin tubing (Section 6.15.2), batteries (Section 6.15.4), gloves (Section 6.7), plastic wrap (Section 6.9), wind suits (Section 6.12), and, if samples are to be filtered, the filtration apparatus (Section 6.14) from the coolers or storage containers in which they are packed.
 - 8.2.8.2 "Clean hands" and "dirty hands" put on the wind suits and PVC gloves (Section 6.7.2).
 - 8.2.8.3 "Dirty hands" removes the pump from its storage bag, and opens the bag containing the SEBS-resin tubing.
 - 8.2.8.4 "Clean hands" installs the tubing while "dirty hands" holds the pump. "Clean hands" immerses the inlet end of the tubing in the sample stream.
 - 8.2.8.5 Both "clean hands" and "dirty hands" change gloves. "Clean hands" also puts on shoulder length polyethylene gloves (Section 6.7.1).

8.2.8.6 "Dirty hands" turns the pump on and allows the pump to run for 5-10 minutes or longer to purge the pump and tubing.

8.2.8.7 If the sample is to be filtered, "clean hands" installs the filter at the end of the tubing, and "dirty hands" sets up the filter holder on the gunwale as shown in Figure 4.

NOTE: *The filtration apparatus is not attached until immediately before sampling to prevent buildup of particulates from clogging the filter.*

8.2.8.8 The sample is collected by rinsing the sample bottle and cap three times and collecting the sample from the flowing stream.

8.2.8.9 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

8.3 Sample Filtration—The filtration procedure described below is used for samples collected using the manual (Section 8.2.5), grab (Section 8.2.6), or jar (Section 8.2.7) collection systems (Reference 7). In-line filtration using the continuous-flow approach is described in Section 8.2.8.7. Because of the risk of contamination, it is recommended that samples for mercury be shipped unfiltered by overnight courier and filtered when received at the laboratory.

8.3.1 Set up the filtration system inside the glove bag, using the shortest piece of pump tubing as is practicable. Place the peristaltic pump immediately outside of the glove bag and poke a small hole in the glove bag for passage of the tubing. Also, attach a short length of tubing to the outlet of the capsule filter.

8.3.2 "Clean hands" removes the water sample from the inner storage bag using the technique described in Sections 8.2.5.2 through 8.2.5.4 and places the sample inside the glove bag. "Clean hands" also places two clean empty sample bottles, a bottle containing reagent water, and a bottle for waste in the glove bag.

8.3.3 "Clean hands" removes the lid of the reagent water bottle and places the end of the pump tubing in the bottle.

8.3.4 "Dirty hands" starts the pump and passes approximately 200 mL of reagent water through the tubing and filter into the waste bottle. "Clean hands" then moves the outlet tubing to a clean bottle and collects the remaining reagent water as a blank. "Dirty hands" stops the pump.

8.3.5 "Clean hands" removes the lid of the sample bottle and places the intake end of the tubing in the bottle.

8.3.6 "Dirty hands" starts the pump and passes approximately 50 mL through the tubing and filter into the remaining clean sample bottle and then stops the pump. "Clean hands" uses the filtrate to rinse the bottle, discards the waste sample, and returns the outlet tube to the sample bottle.

8.3.7 "Dirty hands" starts the pump and the remaining sample is processed through the filter and collected in the sample bottle. If preservation is required, the sample is acidified at this point (Section 8.4).

- 8.3.8 "Clean hands" replaces the lid on the bottle, returns the bottle to the inside bag, and zips the bag. "Clean hands" then places the zipped bag into the outer bag held by "dirty hands."
- 8.3.9 "Dirty hands" zips the outer bag, and places the double-bagged sample bottle into a clean, ice-filled cooler for immediate shipment to the laboratory.

NOTE: *It is not advisable to reclean and reuse filters. The difficulty and risk associated with failing to properly clean these devices far outweighs the cost of purchasing a new filter.*

8.4 Preservation

- 8.4.1 Field preservation is not necessary for dissolved metals, except for trivalent and hexavalent chromium, provided that the sample is preserved in the laboratory and allowed to stand for at least two days to allow the metals adsorbed to the container walls to redissolve. Field preservation is advised for hexavalent chromium in order to provide sample stability for up to 30 days. Mercury samples should be shipped by overnight courier and preserved when received at the laboratory.
- 8.4.2 If field preservation is required, preservation must be performed in the glove bag or in a designated clean area, with gloved hands, as rapidly as possible to preclude particulates from contaminating the sample. For preservation of trivalent chromium, the glove bag or designated clean area must be large enough to accommodate the vacuum filtration apparatus (Section 6.17.3), and an area should be available for setting up the wrist-action shaker (Section 6.17.5). It is also advisable to set up a work area that contains a "clean" cooler for storage of clean equipment, a "dirty" cooler for storage of "dirty" equipment, and a third cooler to store samples for shipment to the laboratory.
- 8.4.3 Preservation of aliquots for metals other than trivalent and hexavalent chromium—Using a disposable, precleaned, plastic pipet, add 5 mL of a 10% solution of ultrapure nitric acid in reagent water per liter of sample. This will be sufficient to preserve a neutral sample to pH <2.
- 8.4.4 Preservation of aliquots for trivalent chromium (References 8-9).
- 8.4.4.1 Decant 100 mL of the sample into a clean polyethylene bottle.
- 8.4.4.2 Clean an Eppendorf pipet by pipeting 1 mL of 10% HCl (Section 7.4.4) followed by 1 mL of reagent water into an acid waste container. Use the rinsed pipet to add 1 mL of chromium (III) extraction solution (Section 7.4.3) to each sample and blank.
- 8.4.4.3 Cap each bottle tightly, place in a clean polyethylene bag, and shake on a wrist action shaker (Section 6.17.5) for one hour.
- 8.4.4.4 Vacuum-filter the precipitate through a 0.4 μm pretreated filter membrane (Section 6.17.2), using fluoropolymer forceps (Section 6.17.1) to handle the membrane, and a 47 mm vacuum filtration apparatus with a precleaned filter holder (Section 6.17.3). After all sample has filtered, rinse the inside of the filter holder with approximately 15 mL of reagent water.

8.4.4.5 Using the fluoropolymer forceps, fold the membrane in half and then in quarters, taking care to avoid touching the side containing the filtrate to any surface. (Folding is done while the membrane is sitting on the filter holder and allows easy placement of the membrane into the sample vial). Transfer the filter to a 30 mL fluoropolymer vial. If the fluoropolymer vial was not pre-equipped with the ultrapure nitric acid (Section 7.4.1), rinse the pipet by drawing and discharging 1 mL of 10% HCl followed by 1 mL of reagent water into a waste container, and add 1 mL of ultrapure nitric acid to the sample vial.

8.4.4.6 Cap the vial and double-bag it for shipment to the laboratory.

8.4.4.7 Repeat Steps 8.4.4.4-8.4.4.6 for each sample, rinsing the fluoropolymer forceps and the pipet with 10% high-purity HCl followed by reagent water between samples.

8.4.5 Preservation of aliquots for hexavalent chromium (Reference 20).

8.4.5.1 Decant 125 mL of sample into a clean polyethylene bottle.

8.4.5.2 Prepare an Eppendorf pipet by pipeting 1 mL of 10% HCl (Section 7.4.4) followed by 1 mL of reagent water into an acid waste container. Use the rinsed pipet to add 1 mL NaOH to each 125 mL sample and blank aliquot.

8.4.5.3 Cap the vial(s) and double-bag for shipment to the laboratory.

9.0 Quality Assurance/Quality Control

9.1 The sampling team shall employ a strict quality assurance/ quality control (QA/QC) program. The minimum requirements of this program include the collection of equipment blanks, field blanks, and field replicates. It is also desirable to include blind QC samples as part of the program. If samples will be processed for trivalent chromium determinations, the sampling team shall also prepare method blank, OPR, and MS/MSD samples as described in Section 9.6.

9.2 The sampling team is permitted to modify the sampling techniques described in this method to improve performance or reduce sampling costs, provided that reliable analyses of samples are obtained and that samples and blanks are not contaminated. Each time a modification is made to the procedures, the sampling team is required to demonstrate that the modification does not result in contamination of field and equipment blanks. The requirements for modification are given in Sections 9.3 and 9.4. Because the acceptability of a modification is based on the results obtained with the modification, the sampling team must work with an analytical laboratory capable of making trace metals determinations to demonstrate equivalence.

9.3 Equipment Blanks

9.3.1 Before using any sampling equipment at a given site, the laboratory or equipment cleaning contractor is required to generate equipment blanks to demonstrate that the equipment is free from contamination. Two types of equipment blanks are required: bottle blanks and sampling equipment blanks.

9.3.2 Equipment blanks must be run on all equipment that will be used in the field. If, for example, samples are to be collected using both a grab sampling device and the jar sampling device,

then an equipment blank must be run on both pieces of equipment.

- 9.3.3 Equipment blanks are generated in the laboratory or at the equipment cleaning contractor's facility by processing reagent water through the equipment using the same procedures that are used in the field (Section 8.0). Therefore, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing equipment blanks at the laboratory or cleaning facility. In addition, training programs must require sampling personnel to collect a clean equipment blank before performing on-site field activities.
- 9.3.4 Detailed procedures for collecting equipment blanks are given in the analytical methods referenced in Table 1.
- 9.3.5 The equipment blank must be analyzed using the procedures detailed in the referenced analytical method (see Table 1). If any metal(s) of interest or any potentially interfering substance is detected in the equipment blank at the minimum level specified in the referenced method, the source of contamination/interference must be identified and removed. The equipment must be demonstrated to be free from the metal(s) of interest before the equipment may be used in the field.

9.4 Field Blank

- 9.4.1 To demonstrate that sample contamination has not occurred during field sampling and sample processing, at least one field blank must be generated for every 10 samples that are collected at a given site. Field blanks are collected before sample collection.
- 9.4.2 Field blanks are generated by filling a large carboy or other appropriate container with reagent water (Section 7.1) in the laboratory, transporting the filled container to the sampling site, processing the water through each of the sample processing steps and equipment (e.g., tubing, sampling devices, filters, etc.) that will be used in the field, collecting the field blank in one of the sample bottles, and shipping the bottle to the laboratory for analysis in accordance with the method(s) referenced in Table 1. For example, manual grab sampler field blanks are collected by directly submerging a sample bottle into the water, filling the bottle, and capping. Subsurface sampler field blanks are collected by immersing the tubing into the water and pumping water into a sample container.
- 9.4.3 Filter the field blanks using the procedures described in Section 8.3.
- 9.4.4 If it is necessary to acid clean the sampling equipment between samples (Section 10.0), a field blank should be collected after the cleaning procedures but before the next sample is collected.
- 9.4.5 If trivalent chromium aliquots are processed, a separate field blank must be collected and processed through the sample preparation steps given in Sections 8.4.4.1 through 8.4.4.6.

9.5 Field Duplicate

- 9.5.1 To assess the precision of the field sampling and analytical processes, at least one field duplicate sample must be collected for every 10 samples that are collected at a given site.
- 9.5.2 The field duplicate is collected either by splitting a larger volume into two aliquots in the glove box, by using a sampler with dual inlets that allows simultaneous collection of two samples,

or by collecting two samples in rapid succession.

- 9.5.3 Field duplicates for dissolved metals determinations must be processed using the procedures in Section 8.3. Field duplicates for trivalent chromium must be processed through the sample preparation steps given in Sections 8.4.4.1 through 8.4.4.6.

9.6 Additional QC for Collection of Trivalent Chromium Aliquots

- 9.6.1 Method blank—The sampling team must prepare one method blank for every ten or fewer field samples. Each method blank is prepared using the steps in Sections 8.4.4.1 through 8.4.4.6 on a 100 mL aliquot of reagent water (Section 7.1). Do not use the procedures in Section 8.3 to process the method blank through the 0.45 µm filter (Section 6.14.1), even if samples are being collected for dissolved metals determinations.

- 9.6.2 Ongoing precision and recovery (OPR)—The sampling team must prepare one OPR for every ten or fewer field samples. The OPR is prepared using the steps in Sections 8.4.4.1 through 8.4.4.6 on the OPR standard (Section 7.4.7). Do not use the procedures in Section 8.3 to process the OPR through the 0.45 µm filter (Section 6.14.1), even if samples are being collected for dissolved metals determinations.

- 9.6.3 MS/MSD—The sampling team must prepare one MS and one MSD for every ten or fewer field samples.

9.6.3.1 If, through historical data, the background concentration of the sample can be estimated, the MS and MSD samples should be spiked at a level of one to five times the background concentration.

9.6.3.2 For samples in which the background concentration is unknown, the MS and MSD samples should be spiked at a concentration of 25 µg/L.

9.6.3.3 Prepare the matrix spike sample by spiking a 100-mL aliquot of sample with 2.5 mL of the standard chromium spike solution (Section 7.4.6), and processing the MS through the steps in Sections 8.4.4.1 through 8.4.4.6.

9.6.3.4 Prepare the matrix spike duplicate sample by spiking a second 100-mL aliquot of the same sample with 2.5 mL of the standard chromium spike solution, and processing the MSD through the steps in Sections 8.4.4.1 through 8.4.4.6.

9.6.3.5 If field samples are collected for dissolved metals determinations, it is necessary to process an MS and an MSD through the 0.45 µm filter as described in Section 8.3.

10.0 Recleaning the Apparatus Between Samples

- 10.1 Sampling activity should be planned so that samples known or suspected to contain the lowest concentrations of trace metals are collected first with the samples known or suspected to contain the highest concentrations of trace metals collected last. In this manner, cleaning of the sampling equipment between samples is unnecessary. If it is not possible to plan sampling activity in this manner, dedicated sampling equipment should be provided for each sampling event.

- 10.2 If samples are collected from adjacent sites (e.g., immediately upstream or downstream), rinsing of the sampling Apparatus with water that is to be sampled should be sufficient.
- 10.3 If it is necessary to cross a gradient (i.e., going from a high-concentration sample to a low-concentration sample), such as might occur when collecting at a second site, the following procedure may be used to clean the sampling equipment between samples:
- 10.3.1 In the glove bag, and using the "clean hands/dirty hands" procedure in Section 8.2.5, process the dilute nitric acid solution (Section 7.2) through the Apparatus.
 - 10.3.2 Dump the spent dilute acid in the waste carboy or in the waterbody away from the sampling point.
 - 10.3.3 Process 1 L of reagent water through the Apparatus to rinse the equipment and discard the spent water.
 - 10.3.4 Collect a field blank as described in Section 9.4.
 - 10.3.5 Rinse the Apparatus with copious amounts of the ambient water sample and proceed with sample collection.
- 10.4 Procedures for recleaning trivalent chromium preservation equipment between samples are described in Section 8.4.4.

11.0 Method Performance

Samples were collected in the Great Lakes during September–October 1994 using the procedures in this sampling method.

12.0 Pollution Prevention

- 12.1 The only materials used in this method that could be considered pollutants are the acids used in the cleaning of the Apparatus, the boat, and related materials. These acids are used in dilute solutions in small amounts and pose little threat to the environment when managed properly.
- 12.2 Cleaning solutions containing acids should be prepared in volumes consistent with use to minimize the disposal of excessive volumes of acid.
- 12.3 To the extent possible, the Apparatus used to collect samples should be cleaned and reused to minimize the generation of solid waste.

13.0 Waste Management

- 13.1 It is the sampling team's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the discharge regulations, hazardous waste identification rules, and land disposal restrictions; and to protect the air, water, and land by minimizing and controlling all releases from field operations.
- 13.2 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* and *Less is Better—Laboratory Chemical Management for Waste Reduction*,

available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

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15.0 Glossary of Definitions and Purposes

These definitions and purposes are specific to this sampling method but have been conformed to common usage as much as possible.

- 15.1 Ambient Water—Waters in the natural environment (e.g., rivers, lakes, streams, and other receiving waters), as opposed to effluent discharges.
- 15.2 Apparatus—The sample container and other containers, filters, filter holders, labware, tubing, pipets, and other materials and devices used for sample collection or sample preparation, and that will contact samples, blanks, or analytical standards.
- 15.3 Equipment Blank—An aliquot of reagent water that is subjected in the laboratory to all aspects of sample collection and analysis, including contact with all sampling devices and apparatus. The purpose of the equipment blank is to determine if the sampling devices and apparatus for sample collection have been adequately cleaned before they are shipped to the field site. An acceptable equipment blank must be achieved before the sampling devices and Apparatus are used for sample collection.
- 15.4 Field Blank—An aliquot of reagent water that is placed in a sample container in the laboratory, shipped to the field, and treated as a sample in all respects, including contact with the sampling devices and exposure to sampling site conditions, filtration, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine whether the field or sample transporting procedures and environments have contaminated the sample.

- 15.5 Field Duplicates (FD1 and FD2)—Two identical aliquots of a sample collected in separate sample bottles at the same time and place under identical circumstances using a duel inlet sampler or by splitting a larger aliquot and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.
- 15.6 Matrix Spike (MS) and Matrix Spike Duplicate (MSD)—Aliquots of an environmental sample to which known quantities of the analytes are added in the laboratory. The MS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations.
- 15.7 May—This action, activity, or procedural step is optional.
- 15.8 May Not—This action, activity, or procedural step is prohibited.
- 15.9 Minimum Level (ML)—The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point (Reference 21).
- 15.10 Must—This action, activity, or procedural step is required.
- 15.11 Reagent Water—Water demonstrated to be free from the metal(s) of interest and potentially interfering substances at the MDL for that metal in the referenced method or additional method.
- 15.12 Should—This action, activity, or procedural step is suggested but not required.
- 15.13 Trace-Metal Grade—Reagents that have been demonstrated to be free from the metal(s) of interest at the method detection limit (MDL) of the analytical method to be used for determination of this metal(s).

The term "trace-metal grade" has been used in place of "reagent grade" or "reagent" because acids and other materials labeled "reagent grade" have been shown to contain concentrations of metals that will interfere in the determination of trace metals at levels listed in Table 1.

**TABLE 1. ANALYTICAL METHODS, METALS, AND CONCENTRATION LEVELS
APPLICABLE TO METHOD 1669**

Method	Technique	Metal	MDL (µg/L) ¹	ML (µg/L) ²
1631	Oxidation/Purge & Trap/CVAFS	Mercury	0.0002	0.0005
1632	Hydride AA	Arsenic	0.003	0.01
1636	Ion Chromatography	Hexavalent Chromium	0.23	0.5
1637	CC/STGFAA	Cadmium	0.0075	0.02
		Lead	0.036	0.1
1638	ICP/MS	Antimony	0.0097	0.02
		Cadmium	0.013	0.1
		Copper	0.087	0.2
		Lead	0.015	0.05
		Nickel	0.33	1
		Selenium	0.45	1
		Silver	0.029	0.1
		Thallium	0.0079	0.02
		Zinc	0.14	0.5
1639	STGFAA	Antimony	1.9	5
		Cadmium	0.023	0.05
		Trivalent Chromium	0.10	0.2
		Nickel	0.65	2
		Selenium	0.83	2
		Zinc	0.14	0.5
1640	CC/ICP/MS	Cadmium	0.0024	0.01
		Copper	0.024	0.1
		Lead	0.0081	0.02
		Nickel	0.029	0.1

¹ Method Detection Limit as determined by 40 *CFR* Part 136, Appendix B.

² Minimum Level (ML) calculated by multiplying laboratory-determined MDL by 3.18 and rounding result to nearest multiple of 1, 2, 5, 10, 20, 50, etc., in accordance with procedures used by EAD and described in the EPA *Draft National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection/Quantitation Levels*, March 22, 1994.

TABLE 2. ANALYTES, PRESERVATION REQUIREMENTS, AND CONTAINERS

Metal	Preservation Requirements	Acceptable Containers
Antimony Arsenic Cadmium Copper Lead Nickel Selenium Silver Thallium Zinc	Add 5 mL of 10% HNO_3 to 1-L sample; preserve on-site or immediately upon laboratory receipt.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Chromium (III)	Add 1 mL chromium (III) extraction solution to 100 mL aliquot, vacuum filter through 0.4 μm membrane, add 1 mL 10% HNO_3 ; preserve on-site immediately after collection.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Chromium (IV)	Add 50% NaOH; preserve immediately after sample collection.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Mercury	Total: Add 0.5% high-purity HCl or 0.5% BrCl to pH < 2; Total & Methyl: Add 0.5% high-purity HCL; preserve on-site or immediately upon laboratory receipt	Fluoropolymer or borosilicate glass bottles with fluoropolymer or fluoropolymer-lined caps

Figure 1 - Grab Sampling Device

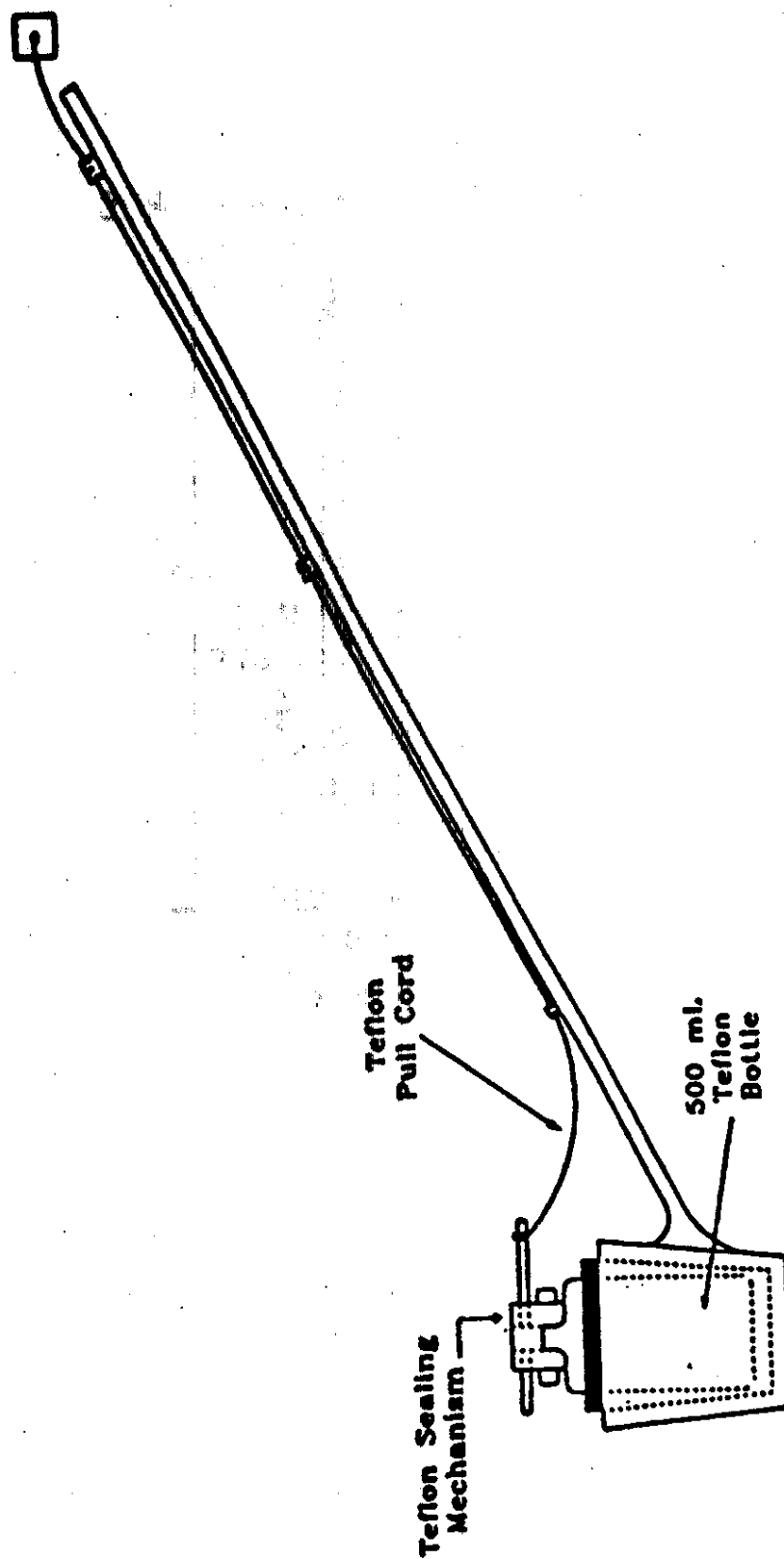


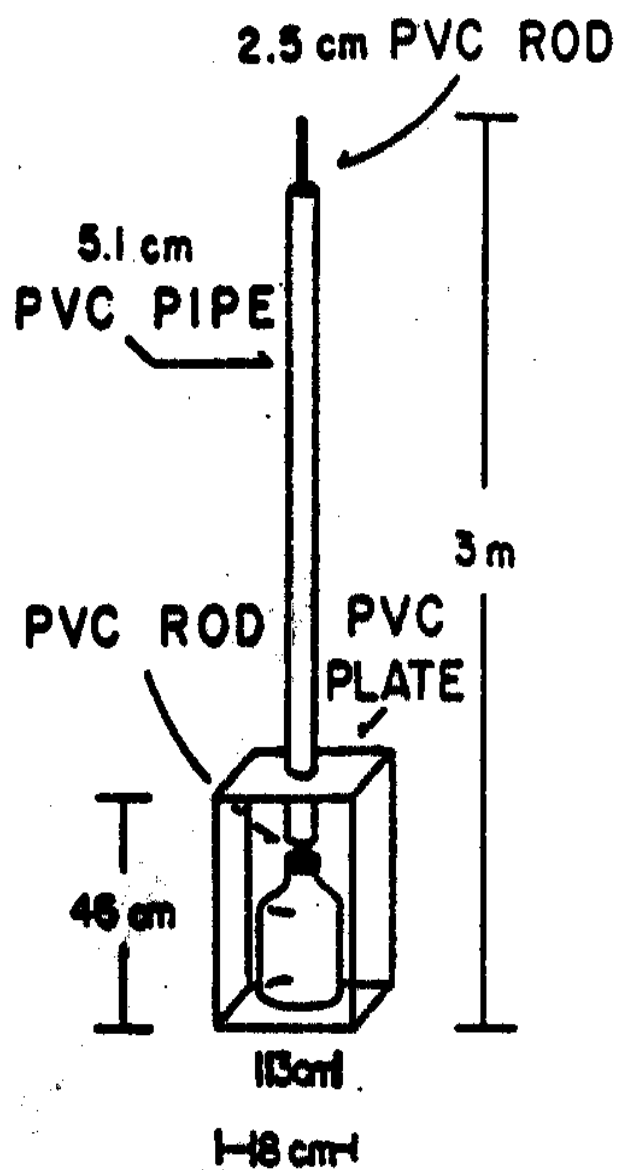
Figure 2 - Grab Sampling Device

Figure 3 - Jar Sampling Device

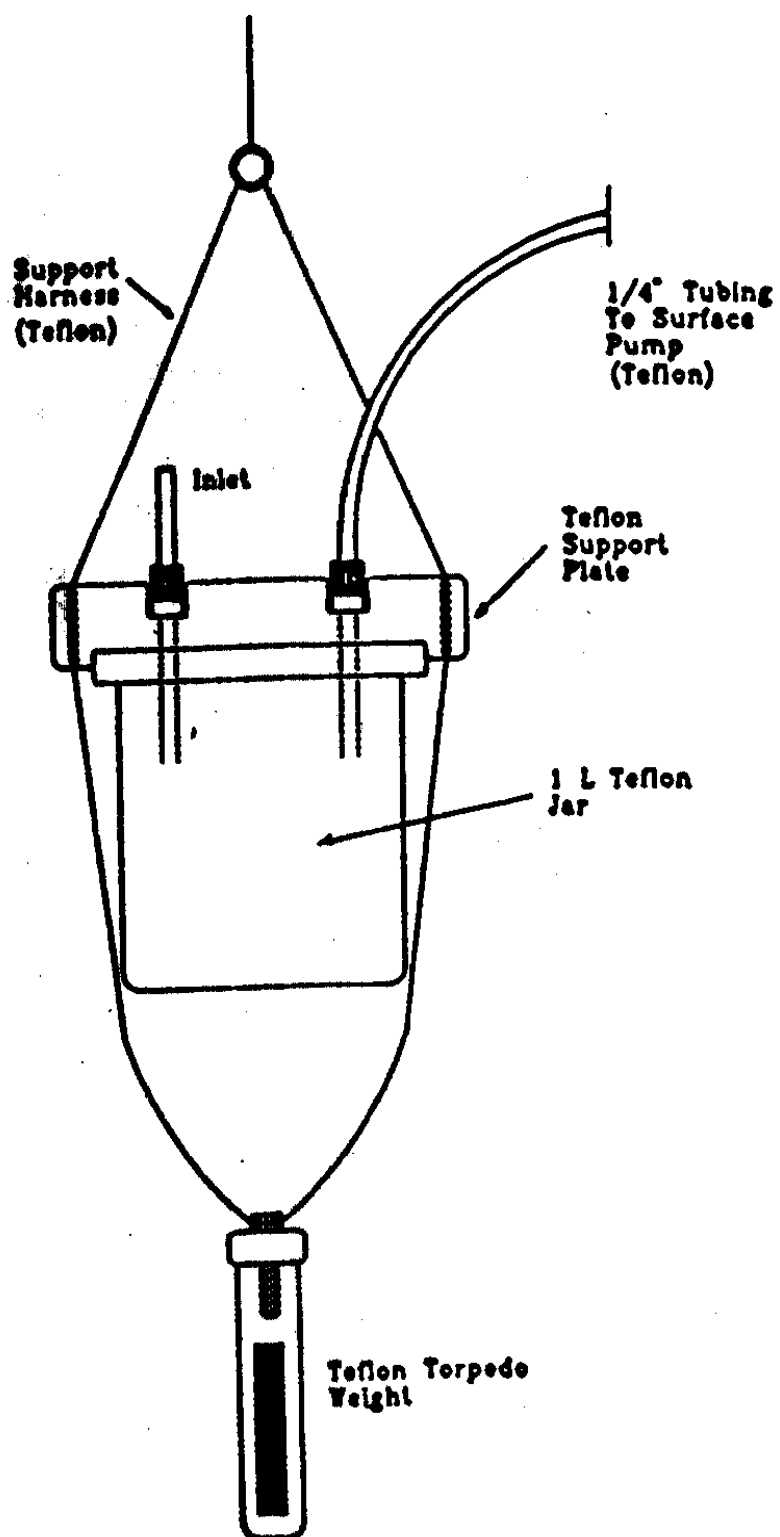
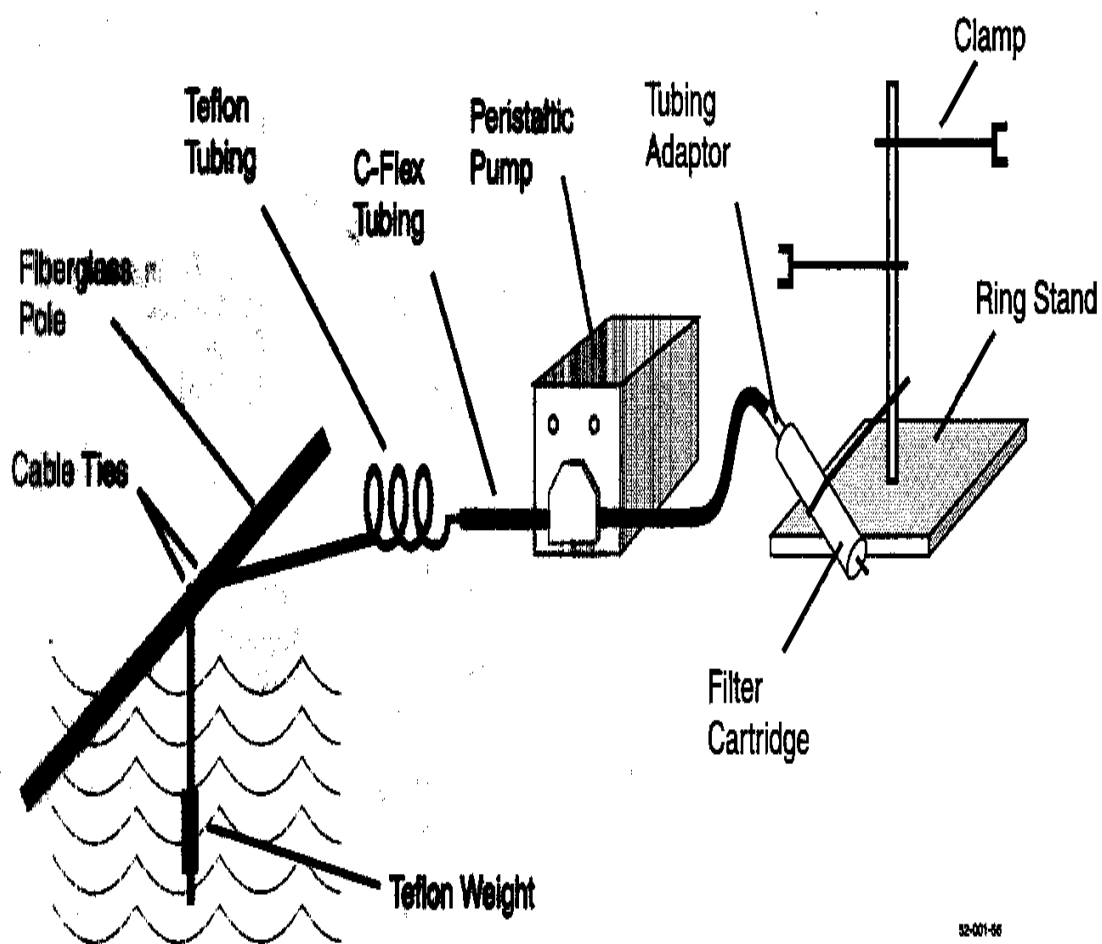


Figure 4 - Sample Pumping System

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